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NEW TECHNOLOGY FOR TREATMENT OF WASTEWATER BY REVERSE OSMOSIS

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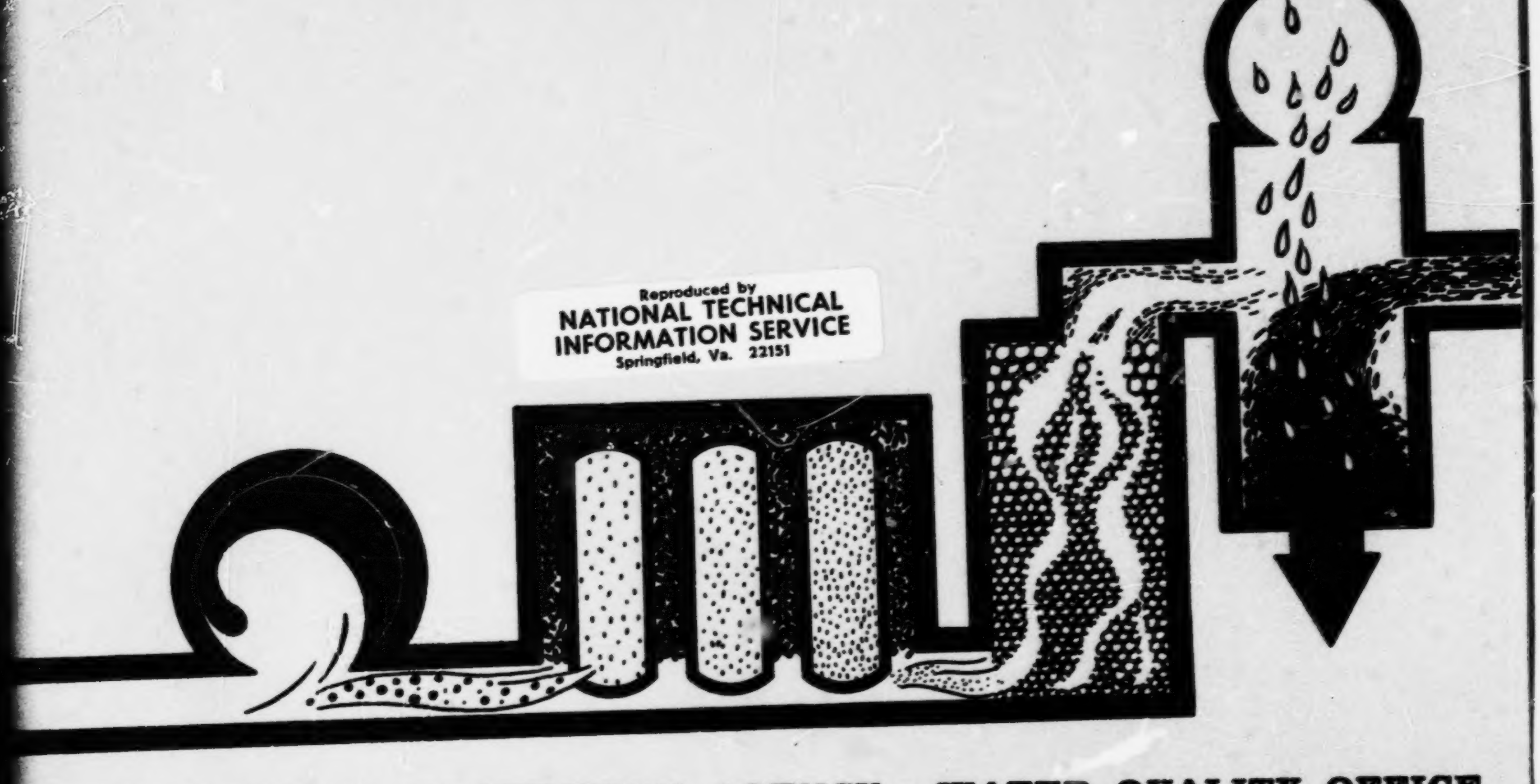

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27 Abstract

Stable, high-flux membranes for wastewater renovation by reverse osmosis were required to meet or exceed: ~~1)~~ fluxes greater than 60 gal/ft²/day with no more than a 20% increase after one year; ~~2)~~ rejection of 60% of sodium chloride; and ~~3)~~ rejection of 90% of sodium sulfate. All testing was performed at 600 psi, with 1000 ppm feed solutions. These specifications were met by three cellulose based membranes. Flux losses over short periods were extrapolated to yearly values and ranged from 12-18%. However, periodic cleaning with a laundry enzyme pre-soak was necessary as the flux rates initially declined very rapidly. Cleaning restored the membranes to 80 to 90% of the initial values. Daily cleaning maintained a five day series of tests at nearly constant levels. The best of the three membranes tested rejected 90 to 97% of TDS, 70 to 100% of COD, 86 to 96% of ammonium ion, 72 to 99% of nitrate ion, and 97 to 99% of total phosphate. Techniques were explored for attachment of proteolytic enzymes to cellulose acetate membranes to render them resistant to colloid fouling. Th proteolytic enzyme trypsin was chemically attached to the active layer surface of a me brane prepared from the N-hydroxysuccinimide ester of cellulose acetate hydrogen succin . The resulting enzymatic membrane displayed hydrolytic activity. No cost estim es were presented for this type of treatment process. (Lowry-Texas)
(WRSIC abstract)

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NEW TECHNOLOGY FOR TREATMENT OF WASTEWATER BY REVERSE OSMOSIS

by

ENVIROGENICS COMPANY
A Division of
Aerojet-General Corporation
El Monte, California 91734

for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

Stable, high-flux membranes were sought for use in the renovation of wastewater by reverse osmosis. Cellulose ester membranes were formulated to produce fluxes greater than 60 gal/ft^2-day which would not decrease by more than 20% after the first year of operation, and reject at least 60% of sodium chloride and 95% of sodium sulfate when tested at 600 psi with 1000 ppm feed solutions.

The target osmotic performance was achieved with each of three membrane types: A cellulose diacetate of moderately-low acetyl content, a cellulose triacetate-diacetate blend, and crosslinked cellulose acetate methacrylate. The intrinsic flux stabilities of these membranes extrapolated to flux losses of only 12 to 18% after the first year of operation.

The fluxes of these high-performance membranes declined rapidly in bench-scale tests with secondary sewage effluent but were restored to within 80 to 90% of the initial values after cleaning with an enzymatic laundry presoak (Biz). Daily cleaning by this technique maintained the fluxes at a nearly constant level over a 5-day test period. The rejection of sewage components by the high-flux membranes was excellent, the best of them rejecting 90 to 97% of TDS, 70 to 100% of COD, 86 to 96% of ammonium ion, 72 to 99% of nitrate ion and 97 to 99% of total phosphate.

Techniques were explored for attachment of proteolytic enzymes to cellulose acetate membranes to render them resistant to colloid fouling. The proteolytic enzyme trypsin was chemically attached to the active layer surface of a membrane prepared from the N-hydroxysuccinimide ester of cellulose acetate hydrogen succinate. The resulting enzymatic membrane displayed hydrolytic activity toward an ester substrate of low molecular weight. The enzyme-polymer compound (in bulk rather than membrane form) also hydrolyzed casein, a model for proteinaceous colloids present in sewage.

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I. CONCLUSIONS

The work carried out during this program has shown that flat-sheet membranes with greatly improved fluxes and excellent flux stability can be fabricated from cellulose esters. At the same time, rejection of organic and ionic constituents adequate for renovation of municipal wastewater by reverse-osmosis was achieved. The best of the high-flux membranes rejected 90 to 97% of TDS, 70 to 100% of COD, 86 to 96% of ammonium ion (at pH 5.00 ± 0.25), 72 to 99% of nitrate ion, and 97 to 99% of total phosphate from secondary effluent at initial fluxes of 50 to 100 gal/ft^2-day (gfd).

The new membranes exhibited flux decline slopes of -0.011 to -0.021 with initial fluxes of 50 to 70 gfd in 200-hr reverse-osmosis tests conducted at 600 psi with 1000 mg/ℓ sodium chloride solution. Flux losses of only 9 to 18% are projected from these flux decline rates after the first year of operation at 600 psi. On the basis of their demonstrated intrinsic flux and flux stability, and excluding the effects of fouling, these membranes are calculated to produce 16,500 to 21,000 gal/ft^2 of product water during the first year of reverse-osmosis operation at 600 psi. These values compare with first-year total water productivity (TWP) of 7000 to 9000 gal/ft^2 calculated for state-of-the-art cellulose diacetate brackish-water membranes produced in these and other laboratories.

Certain of the new membranes exhibited osmotic performance suitable for low-pressure reverse-osmosis operation, which may offer economic advantages over operation at higher pressure. A crosslinked cellulose acetate methacrylate membrane produced a flux of 36 gfd at 200 psi, with no appreciable flux decline, along with 70% salt rejection in a 200-hr test with 1000 mg/ℓ sodium chloride solution. The total water productivity calculated for this membrane over the first year of operation at this pressure is 13,000 gal/ft^2.

Although the new high-flux membranes exhibited excellent flux stability with salt solutions, tests on various sewage effluents demonstrated that membrane fouling is the single most important factor responsible for reduced membrane productivity in the treatment of wastewater. The rate and extent of flux decline appears to depend on the quality of the effluent used, the initial membrane flux, and to a lesser extent, the type of polymer used to fabricate the membrane.

Periodic cleaning with the enzymatic presoak, Biz, during bench-scale reverse-osmosis operation on secondary sewage effluent was shown to be an effective means of maintaining the high flux of the new membranes. For example, in a test conducted at 600 psi with secondary effluent, the fluxes of specially formulated cellulose diacetate membranes were maintained at 40 to 70 gfd over a 6-day period during which the membranes were cleaned every 24 to 48 hrs with Biz solution.

Three membrane types exhibited the excellent performance desired for wastewater treatment. These were Eastman Type E-383-40 cellulose diacetate; a blend of commercial cellulose triacetate (Eastman Type A-432-130B) and diacetate (Eastman Type E-398-3) having an average degree of substitution of 2.55; and a crosslinked cellulose acetate methacrylate.

Chemical attachment of proteolytic enzymes to cellulose ester membranes was investigated as a novel technique for making them resistant to fouling by sewage components. Methods were developed which allow the preparation of membranes from a cellulose acetate containing a reactive functional group capable of surviving the casting and annealing process; and subsequently binding an enzyme covalently. Membranes prepared from the N-hydroxysuccinimide ester of cellulose acetate hydrogen succinate (CAHS-NHS), then treated with trypsin, exhibited 2 to 3% of the esterolytic activity of the native (unattached) enzyme. This degree of activity may be greater than is apparent since the exposed area of the membrane is very small compared with that of the finely divided bulk material. A bulk fibrous preparation of CAHS-trypsin displayed 13 to 17% of the esterolytic activity of the native enzyme and 3% of the activity of the native enzyme toward hydrolysis of casein, a model proteinaceous colloid. This indicated that the enzymatic membranes should display similar activity in catalyzing the breakdown of proteinaceous colloids present in sewage.

The results obtained in a reverse-osmosis test of CAHS membranes with secondary effluent were indicative of an antifouling effect resulting from the negative charge on the CAHS polymer. These results, while preliminary in nature, indicate that membranes carrying a suitable negative surface charge may be resistant to colloid fouling.

II. RECOMMENDATIONS

Excellent results were obtained during this program in the development of new membranes in flat-sheet configuration. The fabrication of high-flux membrane types in tubular form was beyond the scope of the program. A tubular membrane configuration offers advantages for scaled-up operation as well as for flow characteristics. It is therefore recommended that the highly promising membranes based on E-383-40 cellulose acetate and the ds 2.55 blend be developed into high-flux tubes for evaluation against various sewage effluents.

The development of crosslinkable cellulose acetate methacrylate (CAM) membranes in flat-sheet form should be continued, with emphasis on casting these on porous substrates of the type used to line the inside of tubular supports. CAM prepared from the commercially available E-383-40 cellulose acetate should be investigated as a membrane polymer to determine whether membranes fabricated from it will duplicate the outstanding performance of CAM made from a special lot of cellulose diacetate (Type E-360-60).

Further work should be conducted with enzymatic membranes to demonstrate their antifouling properties with sewage effluents. Simple and inexpensive techniques for attachment of enzymes to membranes should also be sought.

Weakly-charged membranes prepared from acidic or basic polymers, or blends of these with cellulose acetate, should be examined for their antifouling properties in tests with sewage effluents.

Some measures to control the effects of fouling, if not the process itself, must be taken in order to realize even a healthy fraction of the high intrinsic water productivity obtainable with suitably formulated cellulose ester membranes. It is therefore recommended that novel methods for the characterization and removal of colloids from wastewater be investigated and that such studies, as well as the use of more conventional techniques such as membrane cleaning and feed pretreatment, be coupled with the testing of high-flux tubular membranes with sewage.

III. INTRODUCTION

The overall objective of this program was to develop improved membranes for renovation of municipal wastewater by reverse osmosis. A major effort was placed on the fabrication of membranes having very high flux with high flux stability and sufficient rejection of sewage components to produce acceptable product water. The goals of osmotic performance were a flux of at least 60 gal/ft^2-day (gfd) with a flux decline of less than 20% (as projected from absolute values of measured flux decline slopes of less than 0.024) in the first year of operation at 600 psi along with moderate rejection of sodium chloride. A secondary objective was to develop membranes inherently resistant to colloid fouling, the factor which appears to be most responsible for flux decline during operation of reverse osmosis units with sewage effluent. Such a high flux and flux stability are needed for economical treatment of wastewater.

Until recently, attainment of fluxes in the desired range was relatively easy, but maintaining them at acceptably high levels over long test periods had not been achieved. Earlier efforts to produce high-flux membranes for desalination of brackish water consisted of reducing the annealing temperatures used in the preparation of cellulose diacetate membranes formulated for the very high salt retention (99% +) necessary for single-pass desalination of seawater. The flux stability of these seawater membranes, however, was dependent on high annealing temperatures (e.g., 90 to 95°C). While the fluxes of such membranes could indeed be increased by lowering the annealing temperature, their flux stability suffered greatly. The high fluxes produced initially by this approach were only transitory and after very short periods of testing declined to values comparable to those of the membranes annealed at higher temperatures.

More recently, a program was undertaken in these laboratories under sponsorship of the Office of Saline Water to investigate more effective ways of attaining stable, high-flux brackish-water membranes.[1] Two very promising approaches to stabilization of the high flux potentially attainable with asymmetric cellulose ester membranes were found as a result of these efforts, and these approaches were applied very successfully during this program to the fabrication of high-flux membranes suitable for wastewater treatment.

The first of these approaches was to attain stable high fluxes through modification of the casting formulation. This method entailed the use of larger amounts of, or more powerful, swelling agents in the formulation than were employed in the case of the older cellulose diacetate seawater membranes. This is believed to effect a higher degree of swelling during the gelation step, and the resulting membranes, due to their high intrinsic water permeability, still produce high fluxes after annealing at high temperatures. An improvement in the flux stability of cellulose diacetate brackish-water membranes was obtained with this fabrication procedure with an attendant increase in long-term total water productivity.

In the second approach, flux stabilization of membranes was achieved by chemical crosslinking. It was felt that crosslinking would serve to lock the polymer chains into position and thus reduce the tendency of the membrane to compact under pressure during reverse-osmosis operation. Such membrane compaction, due to both reversible elastic compression and irreversible plastic creep, was believed to be responsible for most of the flux decline observed with reverse-osmosis membranes during operation under pressure.[2,3] Crosslinking of membranes prepared from cellulose acetate methacrylate (CAM), a mixed cellulose ester containing pendant unsaturation in its chemical structure, was shown to result in a more stable flux.[1] The initial fluxes of the crosslinked CAM membranes, moreover, were higher than those of the corresponding uncrosslinked CAM membranes indicating that resistance to the rapid compaction which occurs immediately on pressurization was increased by crosslinking.

The aim in the development of improved high-flux membranes for wastewater treatment was to achieve maximum flux consistent with both high flux stability and, consequently, high total water productivity over long periods of operation, along with acceptable sewage solute rejection. Membrane productivity was evaluated on the basis of intrinsic membrane flux stability independent of other factors, such as membrane fouling and degradation, which affect flux. The requirements for membrane rejection were felt to be less stringent in general than those for flux and flux stability, because of the low total dissolved solids (TDS) content of domestic sewage, such as sulfate, phosphate, and higher molecular weight organic compounds, which are efficiently rejected by cellulose ester membranes. It was recognized, however, that although moderate TDS rejection is acceptable, the requirements for removal of certain constituents, such as nitrate, ammonia, and soluble COD (which includes lower molecular weight organics) are more demanding. The target rejection properties chosen as criteria for the rapid screening of candidate membranes were 60% rejection of sodium chloride and 95% rejection of sodium sulfate from 1000 mg/ℓ feed solutions. These goals appeared reasonable in view of the high sulfate-to-chloride rejection ratio usually obtained with cellulose acetate membranes, and permitted considerable flexibility in both formulation and choice of polymer during membrane development.

High-flux membranes meeting all of the osmotic performance goals were prepared from each of three polymer types during the program. The choice of these polymer types was based on certain desirable characteristics shown by each, as well as promising results obtained with them in other programs to develop brackish-water desalination membranes. Eastman Type E-383-40 cellulose acetate was an attractive candidate because of the high flux potentially available by virtue of its moderately-low degree of substitution (ds of 2.28 compared with 2.41 for the more commonly used Type E-398-3 cellulose diacetate), and its commercial availability. Blends of cellulose triacetate and diacetate are also based on commercially available polymers (Eastman Type A-432-130B triacetate and E-398-3 diacetate) and membranes produced from them have exhibited generally higher flux stability and salt rejection than those prepared from cellulose diacetate alone.[1,4] Membranes prepared from cellulose acetate methacrylate (CAM) were of particular interest, not only because they could be crosslinked, but because of their very desirable flux and rejection properties. The CAM polymers, prepared by methacrylation of various cellulose acetates, are not now available in commercial quantities but are readily synthesized by established techniques.[1,4]

Covalent attachment of proteolytic enzymes to the surfaces of cellulose acetate membranes was investigated as a novel approach to making them resistant to fouling by colloidal deposits during operation with sewage effluents. It was expected that the attached enzymes could minimize the buildup of flux-depressing deposits by catalyzing the hydrolytic breakdown of colloidal particles present in wastewater when these contacted the membrane surface, or by otherwise interfering with the process of adhesion of the particles to the surface. Since the concentration of colloids in wastewater is on the order of 5 mg/ℓ, the amount and activity of enzymes needed to minimize deposition may be very small.[5] The aim was to develop techniques for the chemical attachment of the enzymes to cellulose acetate without undue loss of enzymatic activity. For this purpose, modified cellulose acetate polymers containing reactive groups capable of binding the enzymes were synthesized and these coupled with the enzymes.

The sensitive chemical nature of most enzymes imposes certain restrictions on the methods used for prepering enzyme-coupled membranes. Most enzymes are readily denatured by heat, although enzymes covalently attached to an insoluble support often show increased heat stability.[6] It therefore seemed unadvisable to attach enzymes to membranes by a scheme which requires the enzyme to undergo the membrane annealing process. Enzymes are also denatured readily on contact with solvents such as alcohols and acetone.[7] The membrane casting procedure would thus be expected to affect adversely the activity of an enzyme coupled to the membrane material.

To avoid the deleterious effects of heat and solvents, two alternatives were considered. In the first of these, the polymer (a modified cellulose acetate) would be prepared with reactive functional groups capable of surviving the casting and annealing temperatures. The reactive membrane would then be treated with an enzyme under mild, aqueous conditions to produce the enzyme-coupled membrane. In the second alternative, a cellulose acetate membrane (or substituted cellulose acetate) would be prepared in the usual way, treated with an "activating" reagent or bifunctional coupling agent, and then coupled with the enzyme. Bifunctional coupling agents pose the problem of crosslinking the cellulosic polymer or the enzyme, while the "activating" reagents, such as cyanogen bromide, may produce a coupling reaction which has not been completely characterized.[8] It appeared particularly important to avoid the uncertainties present in the latter methods since the literature at the outset of this program revealed only one report of an enzyme-coupled membrane, which was prepared by crosslinking papain adsorbed in a collodion membrane.[9] Accordingly, the more complex but better characterized scheme involving a reactive polymer was adopted in the initial exploration.

IV. STABLE, HIGH-FLUX MEMBRANES

Although membranes were fabricated and tested in flat-sheet form throughout the program, fabrication conditions applicable to tube preparation were used where possible with the flat-sheet membranes in anticipation of later development of the most promising formulations into tubes. In the process for producing tubular membranes,[10] used in these laboratories, the membrane is formed by extruding the casting solution onto the inside of a fabric or paper tube at room temperature and gelling the wet film in cold water before any appreciable drying of it occurs. The flat-sheet membranes, accordingly, were cast at room temperature and gelled in water at 1°C within several seconds of casting. The casting and gelation were carried out on 6-in.-wide aluminized Mylar film in a laboratory-scale casting machine. The membranes were cast at a thickness of 10 mils and gelled for a period of 10 min. Annealing (heat-treating) was conducted by immersing the membranes for a period of 3 min in a water bath thermostatted at the specified annealing temperature. After annealing, the membranes were stored in a refrigerator under water in sealed containers until ready for testing.

Reverse-osmosis testing of the flat-sheet membranes was conducted in 3-in. diameter flat-plate test cells* over the 200 to 700 psi pressure range. The test cells and ancillary equipment used has been described in previous reports.[4,11] Three specimens of each membrane were evaluated in all of the tests carried out with salt solutions and sewage, and test data reported are the averages of the individual test specimens.

MEMBRANES FROM CELLULOSE DIACETATE

Eastman Type E-383-40 cellulose acetate was an attractive candidate polymer for development of high-flux membranes because of its moderately low degree of acetyl substitution (ds); its ds value is 2.28 in comparison with a ds of about 2.45 for the cellulose diacetate used in state-of-the-art membranes. Since the intrinsic water permeability of homogeneous films of cellulose acetate of comparable density has been shown to increase with decreasing acetyl ds of the polymer,[1] it was of interest to exploit the high flux potential of this material in membrane development. Cellulose acetate Type E-383-40 has the lowest ds of any of the commercially available cellulose acetate polymers and no previous reports of its use in reverse-osmosis membranes have been found.

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*The cells provide a channel height of 0.007 in. over a 2.7-in. diameter section of exposed membrane. The minimum flow velocity which occurs at the center of the circular flat plate is calculated to be 1.4 ft/sec at 5 GPH circulation rate and 2.8 ft/sec at 10 GPH circulation rate.

A formulation study was carried out with E-383-40 cellulose acetate using acetamide as the swelling agent; acetamide had been found to be very effective in promoting high flux with cellulose triacetate-diacetate blend membranes.[1] In this study, the amounts of acetone and acetamide in the casting solution were varied, and the membranes annealed at temperatures ranging from 80 to 90°C. The reverse-osmosis properties of the membranes prepared from the most promising of these formulations are given in Table 1. The tests were conducted with 1000 mg/l solutions of sodium chloride and sodium sulfate, respectively, at 300 and 600 psi.

The short-term (2-hr) osmotic properties of the membranes cast from formulation 33A and annealed at 80 to 90°C, and those cast from formulation 33B and annealed at 80 to 85°C, were well within the target performance range of the program, with fluxes of 64 to 105 gfd, sodium chloride rejections of 61 to 67% and sodium sulfate rejections of 95 to 98% determined at 600 psi. The membranes annealed at 80°C showed potential for low-pressure (200 to 300 psi) operation producing at 300 psi, fluxes of 42 to 48 gfd with 60 to 66% rejection of sodium chloride. The relatively low sodium sulfate rejections obtained with the high-flux membranes cast from formulation 33C indicated that they contained defects possibly due to overswelling at the higher level of acetamide and lower level of solvent. No further work was done with this formulation.

The intrinsic flux stability of the experimental membranes was assessed by comparison of the flux decline slope, m, defined by the equation $\log J = \log J_1 + m \log t$, where J_1 is the flux after 1 hr of testing and J is the flux at time t. A least means squares analysis of the flux data measured during a nominal 200-hr reverse-osmosis test is used to calculate the value of the slope. In the absence of fouling or membrane degradation the flux decline behavior of membranes appears to obey the linear relationship given by the above equation, on the basis of many long-term tests conducted in these and other laboratories. Integration of the logarithmic equation leads to the following expression for the total water production (TWP) in gallons/ft^2 expected during time t, where t is expressed in hours.

$$TWP = \frac{J_1 t^{m+1}}{24(m+1)}$$

It should be noted that because of the exponential form of both equations, the predicted decline in flux or productivity during the second and subsequent years is very small. For example, a flux decline slope of -0.024 corresponds to a flux loss of 20% during the first year of operation but less than 2% additional loss during the second year.

Long-term (170-hr) tests were conducted at 600 psi with the most promising E-383-40 cellulose acetate membranes to determine their rates of flux decline. The results of these tests, summarized in Table 2, indicate excellent flux stability for these membranes. On the basis of

TABLE 1

OSMOTIC PROPERTIES OF E-383-40 CELLULOSE ACETATE MEMBRANES

	Casting Solution Formulation (parts by weight)		
	33A	33B	33C
E-383-40	10	10	10
Acetone	40	35	32.5
Acetamide	11	11	12
Water	3	3	3
Pyridine	4	4	4

		Osmotic Properties[a]								
		Formulation 33A			Formulation 33B			Formulation 33C		
Annealing Temp., °C	Test Pressure,[a] psi	Flux, gfd	NaCl	Na_2SO_4	Flux, gfd	NaCl	Na_2SO_4	Flux, gfd	NaCl	Na_2SO_4
80	300	42.2	66.3	-	47.7	60.5	-	45.0	59.9	-
	600	105	63.0	96.4	98.0	60.8	96.3	81.3	60.5	85.9
85	300	38.3	72.8	-	32.3	70.5	-	37.3	59.0	-
	600	85.3	66.7	98.2	64.7	65.9	94.5	66.3	65.1	85.3
90	600	64.3	-	97.2	32.0	-	99.0	29.3	-	99.0

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[a] Tested for 2 hrs against 1000 mg/ℓ feed solutions.

TABLE 2

LONG-TERM OSMOTIC PROPERTIES OF E-383-40 CELLULOSE ACETATE MEMBRANES

Casting Formulation[a]	Annealing Temp., °C	One Hour Flux J_1, gfd[b,c]	Flux Decline Slope, m[b,c]	First Year Total Water Production[d] gal/sq. ft.	Salt Rejection, %[b]	
					2 hr	170 hr
33A	85	63.07 ± 0.78	-0.017 ± .003	20,000	74.3	64.4
33A	90	41.50 ± 0.36	-0.016 ± .002	13,400	66.8	72.2[e]
33B	85	66.92 ± 0.88	-0.021 ± .003	20,700	78.4	79.3[e]

---

[a] Formulations given in Table 1.

[b] Determined at 600 psi with 1000 mg/ℓ sodium chloride solution. Duration of test was 170 hrs.

[c] Given by the equation: $\log J = \log J_1 + m \log t$, where J = flux at time t (hrs) and J_1 is the flux after 1 hr.

[d] Calculated from the equation: $TWP = J_1 t^{m+1}/24\ (m+1)$.

[e] pH of feed was maintained at 5.2 ± 0.2.

measured flux decline slopes of -0.016 to -0.021, flux losses due to membrane "compaction" expected during the first year of operation are 13 to 18%. Values of 20,000 to 21,000 gal/ft^2/yr were calculated for the expected total water production (TWP) during the first year of reverse-osmosis operation with the 85°C membranes. These are greatly superior to the productivity values of 7000 to 9000 gal/ft^2/yr calculated for state-of-the-art cellulose diacetate brackish-water membranes from data obtained at 800 psi with 5000 mg/ℓ sodium chloride solution.

A number of test specimens of the 33A and 33B membranes were fabricated and heat-treated at 85°C for testing against sewage effluents. The results of these tests are presented and discussed in a later section entitled "Testing of High-Flux Membranes with Sewage."

CELLULOSE TRIACETATE-DIACETATE BLEND MEMBRANES

The development of high-flux membranes from blends of cellulose triacetate (Eastman Type A-432-130B) and diacetate (Eastman Type E-398-3) was of interest because of the superior flux stability and salt rejection which has been shown by blend membranes formulated for desalination of brackish water in comparison to that of brackish-water membranes prepared from the diacetate alone.[1] Work in this program was directed toward realization of the maximum flux of blend membranes through both modification of the casting formulation and variation of the triacetate-diacetate ratio (and accordingly the average ds), while retaining the intrinsically high flux stability and good rejection properties.

Membranes were cast from the formulation of a 1:1 (by weight) blend of triacetate and diacetate (average ds = 2.63) shown below.

Component	Amount (parts by weight)
A-432-130B	10
E-398-3	10
1,4-Dioxane	55
Acetone	35
Methanol	9
Maleic Acid	3

The casting and gelling procedure employed was the same as that described at the beginning of this section except that the membranes were gelled after a 30-sec drying period. Testing was conducted with a 1000 mg/ℓ TDS mixed feed solution of ionic composition characteristic of that of a typical wastewater. This was done to establish a baseline for further development of blend membranes for wastewater treatment. The membranes were evaluated in the unannealed state to obtain maximum flow.

Both the feed composition and test results are shown in Table 3. The test was conducted for 2-hr periods successively at 200 psi, 700 psi and again at 200 psi. Considerable compaction of this membrane occurred at 700 psi as evidenced by the very small increase in flux produced at this pressure over that produced initially at 200 psi, and by comparison of the initial and final fluxes at 200 psi (before and after testing at 700 psi, respectively). The unannealed blend membrane would best be suited for low pressure operation, where it produces high flux with low chloride rejection but moderate overall rejection. This formulation was not an optimum one for producing stable, high-flux membranes because a low annealing temperature was necessary to obtain the high flux.

Efforts to reformulate the 1:1 blend (ds 2.63) to achieve high flux with high annealing temperature through use of a more potent swelling agent than maleic acid were not successful. Membranes were cast at room temperature from the formulations shown below, gelled in ice water within 1 sec of casting, annealed at 85°C and tested for 2-hr periods at 200 and 600 psi against a mixed feed containing 300 mg/ℓ of sodium chloride and 700 mg/ℓ of sodium sulfate.

Component	Amount (parts by weight)
A-432-130B	10
E-398-3	10
1,4-Dioxane	45
Acetone	35
Methanol	0, 5, 10
Propionamide	8, 10, 12

Most of the membranes appeared overswollen, producing excessive flux with little or no rejection of either solute. The membranes prepared from the formulations containing no methanol and 8 or 10 parts of propionamide produced mediocre flux (7 to 28 gfd at 200 psi and 13 to 53 gfd at 600 psi) and low rejection (9 to 42% of sodium chloride and 36 to 78% of sodium sulfate). The low sodium sulfate rejection was indicative of flaws in these latter membranes. In view of these results, no further work with the 1:1 (ds 2.63) blend was carried out.

Considerably better results were obtained with a blend of 3 parts of cellulose triacetate and 7 parts of cellulose diacetate having an average ds of 2.55. It was theorized that the ds 2.55 blend, by virtue of its lower ds should have higher flux potential and still exhibit the excellent flux stability and rejection behavior characteristic of 1 to 1 blends. This contention was borne out by results obtained with the ds 2.55 blend during the course of the program.

Two formulations of the ds 2.55 blend were examined using a combination of maleic acid and acetamide or propionamide as swelling agents. A

TABLE 3

OSMOTIC PROPERTIES OF UNANNEALED DS 2.63 BLEND MEMBRANES

	Feed[a]			Osmotic Properties[b]		
					Rejection, %	
Pressure, psi	pH	Cl^- Conc., ppm	Conductance, μ mho cm^{-1}	Flux, gfd	Cl^-	Electrical Conductivity
200 (initial)	8.0	178	1180	38.6	50.0	73.1
700	7.6	180	1250	39.2	60.0	77.4
200 (final)	8.9	180	1150	27.0	56.2	77.2

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[a] Nominal feed composition (mg/ℓ): Na^+, 180; Ca^{++}, 80; Mg^{++}, 33; Cl^-, 174; HCO_3^-, 400; $SO_4^=$, 133.

[b] Determined after 2-hr test periods at designated pressures.

series of membranes was cast from these formulations and annealed over the temperature range of 74 to 85°C utilizing the casting and gelling procedure described at the beginning of this section. The reverse-osmosis properties of these membranes tested with 1000 mg/ℓ solutions of sodium chloride and sodium sulfate at 300 and 600 psi were sufficiently close to the target values for the program to warrant further work with this blend. The formulations used and test results obtained are summarized in Table 4. Fluxes of 52 to 72 gfd with 62 to 66% rejection of sodium chloride produced at 600 psi were within the target range, but the somewhat low sodium sulfate rejections of 89 to 91% were indicative of membrane imperfections. The relatively low rejections, particularly of sodium sulfate, exhibited by this first series of ds 2.55 blend membranes were apparently due to the presence of rather large (approximately 100 μm diameter) voids or bubbles which could rupture under pressure producing pinholes. Such holes provide the leakage paths for salt solution which lowers the salt rejection of the membrane. Sodium sulfate rejection of less than 99% is usually an indication of membrane imperfections, since the intrinsic permeability of cellulose acetate membranes toward this solute is very low.

The number and size of the voids in the ds 2.55 blend membranes were reduced considerably by more careful drying of casting solution ingredients, particularly the cellulose triacetate, before preparing the solution. A membrane prepared from a solution of carefully dried ingredients contained very few voids, which were 20 to 30 μm in diameter. This membrane, cast from the 35A formulation, annealed at 85°C and tested with 1000 mg/ℓ salt solutions at 600 psi, produced lower flux (36 gfd) but much higher salt rejection (95% of sodium chloride and 98% of sodium sulfate) than did previous membranes fabricated and tested under the same conditions, but cast from solutions of less carefully dried ingredients.

The flux stability of the ds 2.55 blend membranes fabricated from both of the casting formulations described in Table 4 and annealed at 85°C determined in a long-term (172-hr) reverse-osmosis test conducted at 600 psi with 1000 mg/ℓ sodium chloride solution was outstandingly high.

Casting Formulation	One-Hour Flux, gfd	Flux Decline Slope	Salt Rejection, %	
			2 hr	172 hr
35A	59.14 ± 0.60	-0.013 ± 0.003	69.5	73.1
35C	49.39 ± 0.58	-0.011 ± 0.003	74.5	79.7

The total water production for the first year of operation calculated from this data was 18,500 gal/ft^2 for the 35A membrane and 16,500 gal/ft^2 for the 35C membrane. The results of tests conducted with the ds 2.55 blend membranes on secondary sewage effluent are described later in the section entitled "Testing of High-Flux Membranes with Sewage."

TABLE 4

OSMOTIC PROPERTIES OF DS 2.55 BLEND MEMBRANES

Casting Formulation (parts by wt)	35A	35C
A-432-130B Cellulose Triacetate	6	6
E-398-3 Cellulose Diacetate	14	14
Dioxane	45	45
Acetone	40	40
Maleic Acid	6	6
Acetamide	10	-
Propionamide	-	14

Annealing Temp., °C		Osmotic Properties[a] Formulation 35A Flux, gfd	 Rej., %	 Formulation 35C Flux, gfd	 Rej., %
	Determined with 1000 mg/ℓ Sodium Chloride Solution				
74	300 psi	57.7	46.8	56.2	42.9
	600 psi	101	57.7	92.7	56.0
80	300 psi	40.5	50.1	44.2	47.6
	600 psi	77.0	55.4	72.0	61.9
85	300 psi	25.2	65.6	31.8	56.4
	600 psi	52.3	65.7	54.3	65.8
	Determined with 1000 mg/ℓ Sodium Sulfate Solution				
80	300 psi	38.0	87.2	30.0	90.5
	600 psi	73.0	89.0	55.0	90.7

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[a] Determined after 1- to 2-hr test periods.

CELLULOSE ACETATE METHACRYLATE MEMBRANES

One of the approaches to flux stabilization of membranes investigated in this program was crosslinking. A considerable effort was devoted to fabrication of high-flux membranes from cellulose acetate methacrylate (CAM), a mixed cellulose ester containing unsaturated groups in its chemical structure which serve as crosslink sites. The CAM polymer used for membrane fabrication during the program was synthesized by methacrylation of Eastman Type E-360-60 cellulose acetate (ds 2.09 to 2.12) by an established procedure.[1] This polymer, designated herein as CAM-360, was synthesized in 1000-g batches which had total ds ranging between 2.34 to 2.39 and methacrylyl ds ranging between 0.2 to 0.3. A methacrylate ds in this range is considered sufficiently high to permit adequate crosslinking. This particular CAM polymer was chosen because of its relatively low total ds, compared with the CAM polymers derived from higher ds cellulose acetates such as E-383-40 (ds 2.28) and E-398-3 (ds 2.41), and because of the excellent osmotic properties exhibited by brackish water membranes prepared from it on another program.[1]

As in the case of the blend membranes, CAM-360 membranes formulated for brackish water desalination were tested using the 1000 mg/ℓ six-ion mixed feed described in Table 3, as a starting point in the wastewater membrane development effort. Unlike the cellulose diacetate and blend membranes described in this report, these membranes were cast at -10°C on glass plates and allowed to dry in air for 3 min at this temperature before gelling in water at 1°C. The following casting solution formulation was employed:

Component	Amount (parts by weight)
CAM-360	10
Acetone	40
Water	10
Maleic Acid	14

The membranes were annealed at 80°C and 83°C for 3 min then crosslinked to 93% acetone insolubility by immersion for 3 min at 90°C in a solution containing 0.035 M of potassium persulfate and 0.040 M of sodium bisulfite using a previously described procedure.[4] The degree of acetone insolubility of a crosslinked CAM membrane is an indication of how completely the crosslinking reaction has taken place since crosslinking of a polymer insolubilizes it. The acetone insolubility of a membrane is determined by measuring the loss in weight occurring after it is stored for several hours at room temperature in the solvent.

Short-term reverse osmosis tests were conducted on the CAM-360 membranes at 200 and 700 psi with a 1000 mg/ℓ mixed feed solution similar to that used with the unannealed blend membrane described previously (see Table 3). The osmotic properties of these crosslinked CAM membranes as shown by the data in Table 5 were characterized by very high flux (70 to 90 gfd at 700 psi) with relatively high chloride rejection (80 to 90%) and somewhat higher total dissolved solids (TDS) rejection as measured by electrical conductivity. The nearly proportionate increase in flux produced by the membranes with increased test pressure was indicative of high resistance to compaction, particularly so with the membrane annealed at 83°C.

It was of interest to determine the maximum flow obtainable with the crosslinked CAM-360 membranes while maintaining salt rejection and flux stability within an acceptable range. Such information would also establish the potential for development of very high flux CAM membranes suitable for low pressure operation. For this purpose, additional specimens of membranes cast at -10°C from the formulation described above were annealed at lower temperature, 74 and 77°C, respectively, crosslinked to 85 to 90% acetone insolubility by the same procedure used with the membranes annealed at 80°C and 83°C, and tested for 200 hrs at 200 psi against a feed containing 292 mg/ℓ of sodium chloride and 708 mg/ℓ of sodium sulfate. The test results, summarized below, indicate that very high fluxes can be obtained at low pressures, together with suitable salt retention.

Annealing Temp., °C	One-Hour Flux, gfd	Flux Decline Slope	Rejection, %	
			NaCl	Na_2SO_4
74	61.7	-0.015	67.2	96.0
77	49.0	-0.015	76.5	95.5

Although exhibiting excellent osmotic properties for wastewater treatment, these CAM membranes were fabricated under conditions (cast at -10°C, with long drying time before gelation) unsuitable for development of tubular membranes. Consequently, CAM-360 was reformulated for room temperature casting and gelling within several seconds of casting, the conditions which prevail in the extrusion of tubular membranes. Two basic formulations were examined, one based on maleic acid/water as the swelling agent/non-solvent combination (similar to the formulation used in preparation of the CAM membranes described above) and the other utilizing acetamide/water for this purpose. A series of membranes was prepared from each basic formulation in which the amount of acetone was varied. The solvent level (i.e., polymer concentration) in the casting solution sometimes has a marked effect on the properties of the resulting membranes. The membranes were all annealed at 74°C and tested without crosslinking at 300 psi and 600 psi against 1000 mg/ℓ sodium chloride solution. The formulations and test results are summarized in Table 6. The most notable observation with these results was the difference in flux and rejection behavior with increased pressure between the maleic acid and acetamide formulations. The membranes cast from the maleic acid formulations (Nos. 32A through 32D, Table 6) exhibited a marked drop in salt rejection when the test pressure was increased with a flux increase proportionately higher than the pressure increase, particularly at the

TABLE 5

OSMOTIC PROPERTIES OF CROSSLINKED CAM-360 MEMBRANES CAST AT -10°C

		Feed[a]			Osmotic Properties[b]		
						Rejection, %	
Annealing Temp., °C	Pressure, psi	pH	Cl⁻ Conc., ppm	Conductance, μmho cm^{-1}	Flux, gfd	Cl⁻	Electrical Conductivity
80	200	8.3	180	1190	32.7	85.2	88.5
80	700	7.4	200	1180	91.3	81.1	84.1
83	200	8.3	180	1190	22.2	89.5	93.0
83	700	7.4	200	1180	70.0	88.0	91.8

---

[a] Nominal feed composition(mg/ℓ): Na^+, 180; Ca^{++}, 80; Mg^{++}, 33; Cl^-, 174; HCO_3^-, 400; $SO_4^=$, 133.

[b] Determined after 2-hr test periods at designated pressures.

TABLE 6

REFORMULATION OF CAM-360 MEMBRANES FOR ROOM-TEMPERATURE CASTING

		Casting Solution Formulation (parts by wt.)[a]						
		32A	32B	32C	32D	32E	32F	32G
CAM-360		10	10	10	10	10	10	10
Acetone		40	35	32.5	30	40	35	32.5
Maleic Acid		14	14	14	14	-	-	-
Acetamide		-	-	-	-	8	8	8
Water		10	10	10	10	5	5	5
		Osmotic Properties[b]						
300 psi	Flux, gfd	23.5	25.5	21.0	22.7	23.5	33.7	53.5
	Rej., %	85.9	87.8	89.0	87.6	78.5	27.8	8.9
600 psi	Flux, gfd	57.8	55.3	131	79.0	53.3	55.7	74.7
	Rej., %	69.4	78.7	32.1	56.0	83.3	35.9	11.4

---

[a] Membranes cast at room temperature, gelled at 1°C within 1 sec of casting and annealed at 74°C. Membranes were not crosslinked.

[b] Determined after 2 hrs test time at the designated pressures with 1000 mg/ℓ sodium chloride solution.

lower solvent levels. This is indicative of the rupture of voids at the higher pressure. Formulation 32B, however, yielded a membrane which decreased only moderately in salt rejection on high pressure operation. In contrast, the salt rejection of all the acetamide membranes (formulations 32E through 32G, Table 6) increased with pressure and their fluxes increased with pressure in a more normal behavior for reverse-osmosis membranes. Promising results were obtained with the acetamide formulation at an acetone level of 40 parts per 10 parts of polymer. The low rejections obtained with the membranes cast from solutions containing less solvent were apparently due to pinhole defects which formed during their fabrication rather than during operation since the rejections were low even at the low pressure.

Additional CAM-360 membranes were cast from the maleic acid and acetamide-based formulations 32B and 32E, respectively, to determine the range of flux and salt rejection obtainable with uncrosslinked membranes fabricated under these conditions. In contrast to the first series, these membranes were cast at room temperature, dried for a few seconds, and annealed at low temperatures (50 to 70°C). This second series of membranes exhibited very desirable osmotic properties as shown by the results of short-term tests conducted at 300 psi and 600 psi with 1000 mg/ℓ sodium chloride and sodium sulfate solutions, summarized in Table 7. Fluxes of 71 and 88 gfd with sodium chloride rejections of 75 and 65% produced at 600 psi by the membranes annealed at 60°C and 50°C were well within the program performance goals. The 60°C membranes when tested against sodium sulfate solutions gave high (90 to 97%) rejection of this solute. These membranes were cast from the same batch of casting solution used to prepare the 60°C membranes tested with sodium chloride solution but were annealed and tested separately from the latter. The higher fluxes produced with the sodium sulfate feed may have been due to random variations in annealing temperature and test pressure. The 50°C membrane showed potential for low pressure operation, producing 56 gfd flux with 66% sodium chloride rejection at 300 psi.

Contrasting behavior of flux and salt rejection with increasing test pressure was again exhibited by the two formulations - the maleic acid formulation showing a decrease in salt rejection while the acetamide formulation showed a slight increase in rejection. This difference in behavior is attributed to differences in the void structures of the two types of membranes. Voids, as described in the previous section on blend membranes, are bubbles or cavities present in the microporous membrane substructure which are large in size compared to the thickness of the dense active layer of the membrane, and which form during the gelation or desolvation step in membrane fabrication. They occur very commonly in asymmetric reverse-osmosis membranes and can impair membrane performance by rupturing when the membrane is pressurized. The microporous substructure provides ample mechanical support for the active layer at the pressures commonly employed in reverse-osmosis operation. The presence of large voids very close to the active layer surface, however, causes weak spots in that surface. Failure at these weak points usually occurs under pressure to produce holes or breaks in the active layer which leak salt solution, and subsequently, reduces salt rejection.

TABLE 7

EFFECT OF ANNEALING TEMPERATURE ON OSMOTIC PROPERTIES OF CAM-360 MEMBRANES CAST AT ROOM TEMPERATURE

Annealing Temp., °C	Test Pressure, psi	Osmotic Properties[a]			
		32B[b]		32E[b]	
		Flux, gfd	Rej., %	Flux, gfd	Rej., %
Determined with 1000 mg/ℓ Sodium Chloride Solution					
74	300	25.5	87.8	28.5	78.5
	600	55.3	78.7	53.3	83.3
70	300	27.8	84.5	21.8	86.6
	600	53.3	82.1	43.3	89.6
60	300	41.0	78.0	45.0	64.0
	600	70.7	74.6	71.3	68.9
50	300	56.3	65.6	-	-
	600	88.2	64.9	-	-
Determined with 1000 mg/ℓ Sodium Sulfate Solution[c]					
60	300	55.3	97.3	52.0	93.8
	600	98.7	90.0	84.0	96.3

---

[a] Determined after 2 hrs of testing at the pressures and with the feeds designated.

[b] Formulation given in Table 6. Membranes cast at room temperature and gelled within 1 sec of casting. Membranes were not crosslinked.

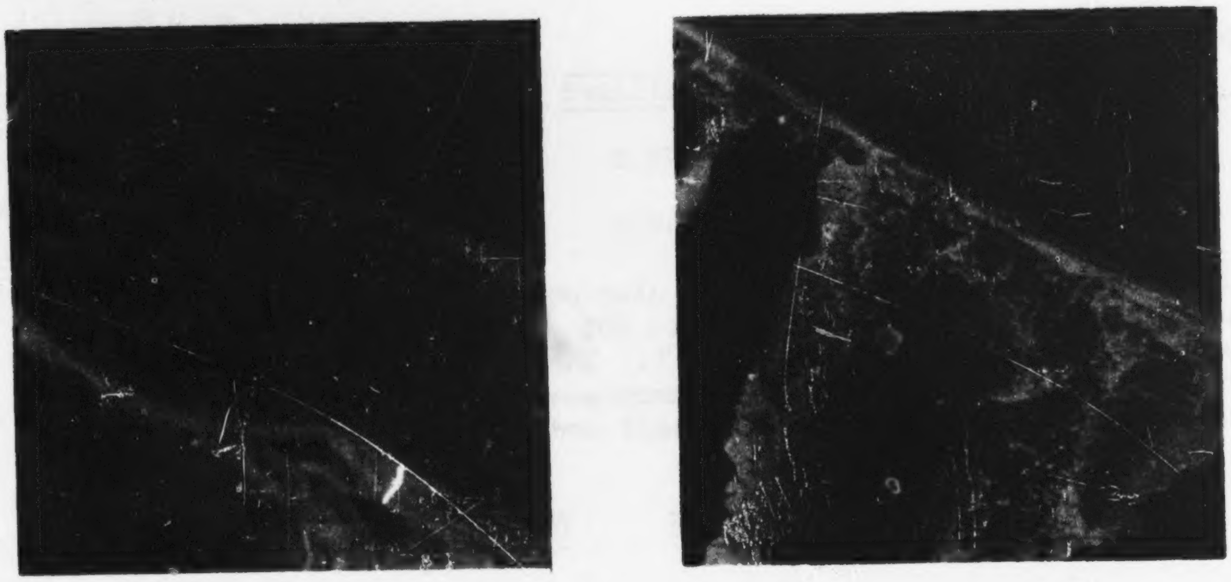
[c] Membranes were annealed separately from those tested with sodium chloride solution.

The CAM-360 membranes prepared from either formulation contained numerous small (1 to 10 micrometer diameter) and large (20 to 30 micrometer diameter) voids, as shown in Figure 1 by the scanning electron micrographs of the maleic acid (formulation 32B) and acetamide (formulation 32E) membranes. In the former membranes, large voids are seen to be situated very close to the active layer (top) surface. These membranes exhibited a drop in salt rejection and disproportionately large increase in flux with increased pressure, which behavior is indicative of void rupturing. In contrast, the voids, particularly the larger ones, in the acetamide membrane were located further beneath the active layer surface, and these membranes showed no evidence of void rupturing at the higher test pressure (see data of Tables 6 and 7). These differences are brought out particularly well by the data obtained with the 1000 mg/ℓ sodium sulfate feed and shown in Table 7. The rejection of this solute decreased from 97 to 90% with the 32B membrane while increasing from 94 to 96% for the 32E membrane when the test pressure was increased from 300 to 600 psi.

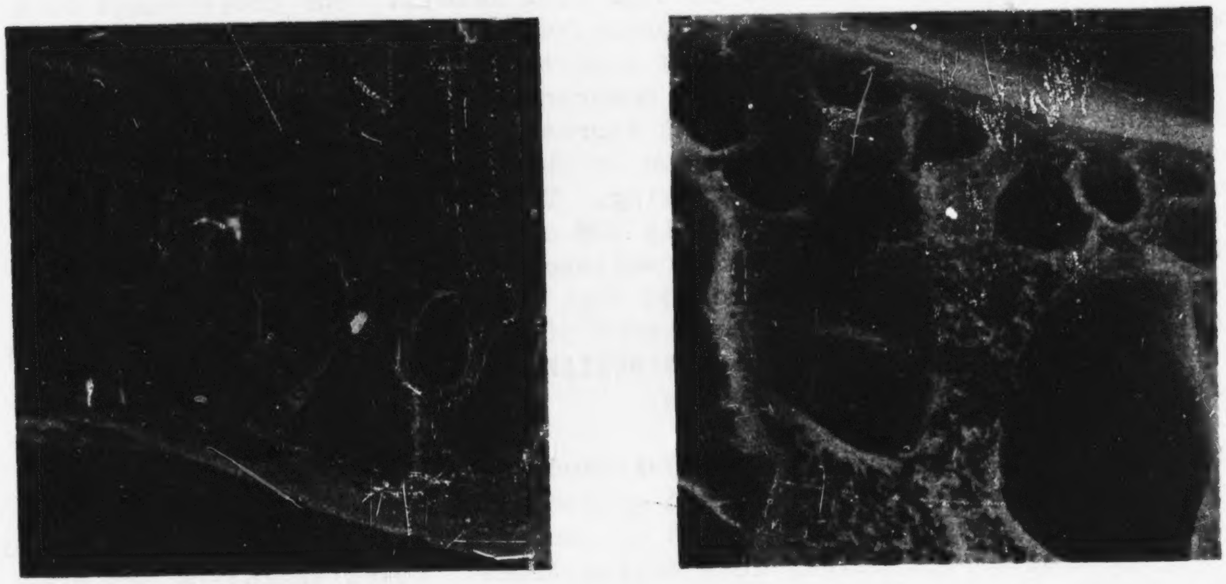
Although the mechanism of void formation is not yet well understood, it has been established from work accomplished under other programs,[1,4,12,13] that void frequency, size, shape and location in a membrane are greatly dependent upon a number of factors, such as formulation, fabrication conditions and polymer type. Much progress has been made in the control of void formation through modifications in membrane formulation and fabrication conditions and the problem does not appear to be a limiting one in the development of membranes for wastewater treatment. A detailed study of this phenomenon was beyond the scope of this program, but its importance to membrane performance is borne out by the observations described above for the CAM-360 membranes, and in the previous section for the ds 2.55 blend membranes.

Crosslinking of the CAM-360 membranes cast at room temperature from the 32B (maleic acid-based) and 32E (acetamide-based) formulation described above (see Tables 6 and 7) and annealed at 60°C was attempted using the procedure employed previously with the membranes cast at -10°C and annealed at higher temperature. This procedure was unsatisfactory for treatment of the reformulated membranes because of excessive shrinkage and deformation which occurred. Treatment of the membranes for 4 to 12-hr periods at room temperature in the crosslinking solution rather than 90°C was also unsatisfactory because of apparent membrane degradation, evidenced by excessive flux and low salt rejection (e.g., 50% rejection of sodium sulfate).

Acceptable crosslinking was finally achieved by immersion of the membranes in the persulfate-bisulfite bath at the temperature at which the membranes had been annealed for periods of 5 to 20 min, depending upon the temperature. The results of 1-hr reverse-osmosis tests conducted at 300 and 600 psi with 1000 mg/ℓ sodium sulfate solution with uncrosslinked and crosslinked CAM-360 membranes cast from the 32E formulation (at room temperature with short drying time before gelation) and annealed at 60°C are summarized below. The membranes were crosslinked to 60% acetone insolubility by immersion for 15 min at 60°C in the persulfate-bisulfite bath.



32B (Maleic Acid) Formulation



32E (Acetamide) Formulation

50 micrometer
10 micrometer

Figure 1. Void Structure of CAM-360 Membranes

Test Pressure, psi	Flux, gfd		Na_2SO_4 Rejection, %	
	Uncrosslinked	Crosslinked	Uncrosslinked	Crosslinked
300	52.0	78.0	93.8	98.5
600	84.0	144.0	96.3	98.3

Excellent osmotic properties were also obtained with similar membranes annealed at 70°C and crosslinked to 60% acetone insolubility by treatment in the bath for 10 min at 70°C. The results of 1-hr tests conducted with these latter CAM-360 membranes both uncrosslinked and crosslinked at 600 psi with 1000 mg/ℓ sodium chloride are given below.

Flux, gfd		NaCl Rejection, %	
Uncrosslinked	Crosslinked	Uncrosslinked	Crosslinked
43.3	73.3	89.6	91.7

The short-term osmotic properties of the crosslinked CAM-360 membranes described above were extremely promising, particularly in view of the high salt rejections obtained at high flux levels. The crosslinked 60°C membranes appeared ideal for low-pressure (e.g., 200 psi) operation. Crosslinking of these membranes is seen to have greatly increased their fluxes (72% increase for the 60°C membrane and 69% increase for the 70°C membrane at 600 psi) with a slight increase in salt rejection. This behavior is attributed to an increase in the compaction resistance of the membranes as a result of crosslinking. The relatively low degree of acetone insolubility (approximately 60% compared with 85 to 93% obtained earlier with CAM-360 membranes crosslinked at 90°C) found for these membranes after crosslinking indicated that the crosslinking procedure warrants further improvement. The degree of crosslinking achieved, however, evidently provided adequate flux stabilization, as shown by the results of long-term tests described below.

The osmotic properties of the crosslinked CAM-360 membranes fabricated by casting at room temperature and gelled within seconds of casting compared very favorably with those of the earlier membranes cast at -10°C and gelled after relatively long drying times. Lower annealing temperatures were required with the former than with the latter membranes to achieve the same flux. The crosslinked CAM-360 membranes, in general, exhibited higher salt rejection at a given flux level than did the E-383-40 cellulose acetate and ds 2.55 blend membranes.

The flux stability of the crosslinked CAM-360 membranes fabricated at room-temperature, under short drying time conditions was determined in long-term (nominal 200-hr) tests conducted at 200 and 600 psi with 1000 mg/ℓ sodium chloride solution. The 32B and 32E membranes annealed and crosslinked at 70°C were tested at 600 psi and a 32E membrane processed at 60°C was tested at 200 psi. The results are summarized in Table 8. The

TABLE 8

LONG-TERM OSMOTIC PROPERTIES OF CROSSLINKED CAM-360 MEMBRANES CAST AT ROOM TEMPERATURE

Casting Formulation[a]	Annealing Temp., °C	Percent Acetone Insoluble	Test Pressure, psi	One Hour Flux, gfd[b]	Flux Decline Slope[b]	First Year Total Water Production, gal/sq. ft.	Salt Rejection, %[b] 2 hr	Salt Rejection, %[b] 175 hr
32E	60[c]	58	200	35.52 ± 0.51	-0.001 ± 0.004	12,800	70.1	68.8
32E	70[d]	65	600	63.19 ± 0.72	-0.020 ± 0.003	19,700	87.2	87.0
32B	70[d]	29	600	73.36 ± 1.19	-0.054 ± 0.004	17,400	74.7	75.5

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[a] Formulations given in Table 6

[b] Determined with 1000 mg/ℓ sodium chloride solution. Duration of test was 175 hrs.

[c] Membrane crosslinked by immersion for 15 min at 60°C in a solution of $K_2S_2O_8$ (0.035 M) and $NaHSO_3$ (0.040 M).

[d] Membranes crosslinked as in c except for 10 min at 70°C. Both membranes treated simultaneously in same bath.

membranes prepared from formulation 32E (based on acetamide) showed excellent flux stability, under the test conditions employed, well within the program performance goal (absolute value of flux decline slope less than 0.024). The 60°C membrane, when tested at 200 psi, showed, for all practical purposes, no flux decline, and the value of 13,000 gal/ft^2 for the first year's total water productivity, calculated for this membrane compares very favorably with values at 800 psi of 7000 to 11,000 gal/ft^2 calculated for current cellulose diacetate and 1:1 blend brackish-water membranes operating on 5000 mg/ℓ sodium chloride. The performance of the crosslinked 32E membrane (70°C) at 600 psi was outstanding in terms of combined high water productivity and high salt rejection.

The difference in flux stability observed between the crosslinked 70°C membranes prepared from the 32B formulation (based on maleic acid) and the 32E formulation (based on acetamide) was evidently due to the difference in their extent of crosslinking. The 32B membrane was the less stable of the two, with a flux decline of -0.054 compared with a slope of -0.020 for the 32E membrane. The former had an acetone-insoluble fraction of only 29% compared with 65% insolubility of the latter membrane. These differences and their interrelationships were quite clear-cut in view of the fact that both membranes were crosslinked under identical conditions in the same bath. A possible explanation of the inferior results with the 32B membrane is that chemical degradation took place either due to residual maleic acid or during the crosslinking treatment through acid-catalyzed hydrolysis of the methacrylate groups. Such degradation of CAM-360 has been observed with solutions of the 32B formulation after storage at room temperature for periods of a week or more.

The results obtained with both crosslinked and uncrosslinked CAM-360 membranes point up the superiority of the acetamide-based formulation over the maleic acid-based formulation in terms of osmotic properties and ease of crosslinking of flat-sheet membranes, fabricated under conditions applicable to extrusion of tubular membranes. The outstanding performance obtained with the membranes prepared from this formulation was very encouraging and indicated high potential for development of practical CAM membranes for wastewater treatment. The results of tests conducted with CAM-360 membranes against secondary sewage effluent are discussed in the next section.

V. TESTING OF HIGH-FLUX MEMBRANES WITH SEWAGE

The best flat-sheet membranes developed from each of the three polymer types examined during the program were evaluated against sewage effluents obtained from the Pomona Water Reclamation Plant, Pomona, California. The tests were conducted at 600 psi for periods of 5 to 17 days in 3-in. flat-plate test cells, constantly recirculating the feed from a 5-gal reservoir. Except for two cases where primary and carbon-treated secondary effluents were employed as feeds, all of the tests were conducted with untreated secondary effluent. The pH of the sewage feeds was maintained at 5.00 ± 0.25 by the addition of dilute sulfuric acid. Five milliliters per gallon of 5% sodium hypochlorite solution was also added to each feed batch as a routine measure. Each batch of sewage effluent used at the start of the tests and to replenish the feed during the tests was obtained from the water reclamation plant the morning of the same day that it was used. Variation of the feed composition during tests in which the feed was replaced periodically with fresh effluent, then, reflected day-to-day variations in effluent quality originating at the reclamation plant. In each test, the feed and product were analyzed for electrical conductivity, chloride ion, TDS (by residue on evaporation), COD (total and "soluble"), nitrate ion, ammonium ion (as NH_3) and total phosphate. The electrical conductivity and chloride ion concentrations were measured twice daily and the concentrations of the other constituents determined in most cases daily. "Soluble" COD in the feed was determined on the filtrate after passage of the feed through a 0.45 micrometer (μm) Millipore filter. The reverse-osmosis test loop employed contained six test cells. Three specimens of each membrane were tested in each case (except in Test No. 6 where two test specimens were used for each membrane evaluated) and the results reported were the averages of each set of three test circles. Prior to testing with sewage, the membranes were tested (at 600 psi) with 1000 mg/ℓ sodium chloride solution, and in several cases with 1000 mg/ℓ sodium sulfate solution, to determine their intrinsic flux and rejection properties. These values provided a reference point for judging rejection behavior and rate and extent of flux declines with the sewage feeds.

Preliminary tests with Pomona secondary effluent were conducted for 5 to 6-day periods using E-383-40 cellulose acetate membranes cast from two promising formulations (those designated 33A and 33B in Table 1) and annealed at 85°C. Specimens of these membranes had previously exhibited excellent osmotic properties and flux stability when tested with 1000 mg/ℓ sodium chloride solution, as shown by the data in Table 2. The purpose of these first tests with secondary effluent was to observe the rate and extent of flux decline due to fouling and the rejection of organic and inorganic sewage components. The results of these tests, designated Test Nos. 1 and 2 are summarized in Tables 9 and 10. The composition of the sewage feeds, determined during each day of the tests (except for the weekends), are given in Table 11. In Test No. 1, the sewage feed was recirculated through the test cells at a rate of 5 GPH and allowed to concentrate over the duration of the test to the point at which its electrical conductivity had increased to approximately twice the original value. In Test No. 2 and all subsequent tests, the feed was recirculated

TABLE 9

TESTING OF E-383-40 CELLULOSE ACETATE MEMBRANES WITH POMONA SECONDARY EFFLUENT

TEST NUMBER 1

Test Time, Days	Flux,[a] gfd	Rejection, %						
		Electrical Conductivity[a]	TDS[b]	Cl^-[a]	COD[b,c]	NH_4^+[b]	NO_3^-[b]	Total Phosphate[b]
Membrane A[d] - Initial Osmotic Properties[e]: 73 gfd flux, 64% rejection								
Start (2 hrs)	49	87	-	-	-	-	-	-
1	31	89	93	75	98	91	33	97
2	26 → 29[f]	89	91	70	>99	77	55	98
5	12	80	-	47	91	62	62	95
6	9	79	-	-	81	77	8[g]	94
Membrane B[d] - Initial Osmotic Properties[e]: 57 gfd flux, 72% rejection								
Start (2 hrs)	48	89	-	-	-	-	-	-
1	31	92	94	78	98	92	33	99
2	29 → 32[f]	91	93	75	>99	85	55	99
5	13	86	-	60	77	70	40	97
6	10	83	-	-	86	80	8[g]	96

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[a] Determined at 600 psi with 5 GPH feed circulation velocity. Values reported are the averages of morning and afternoon samplings.

[b] One sampling per day carried out. TDS determined as residue on evaporation.

[c] Based on feed filtered through 0.8 μm Millipore filter.

[d] Formulations were those of 33A (Membrane A) and 33B (Membrane B) given in Table 1. Both membranes annealed at 85°C.

[e] Determined at 600 psi with 1000 mg/ℓ sodium chloride solution after 1 hr of testing.

[f] Flux increased to this value when feed circulation velocity was increased to 10 GPH for 1 hr.

[g] Low values probably due to faulty analytical results.

TABLE 10

TESTING OF E-383-40 CELLULOSE ACETATE MEMBRANES WITH POMONA SECONDARY EFFLUENT

TEST NUMBER 2

Test Time, Days[a]	Flux, gfd[b]	Rejection, % Electrical Conductivity[b]	TDS[c]	Cl^-[b]	COD[c,d]	NH_4^+[c]	NO_3^-[c]	Total Phosphate[b]
Membrane A[e] - Initial Osmotic Properties[f]: 83 gfd flux, 70% rejection								
Start (1 hr)	57	92	-	77	-	-	-	-
1	28	92	89	74	83	88	31	99
2	18	90	-	-	-	-	-	-
4	15	88	73	73	-100	77	50	95
5	15	90	93	66	83	91	35	97
Membrane B[e] - Initial Osmotic Properties[f]: 57 gfd flux, 82% rejection								
Start (1 hr)	45	95	-	85	-	-	-	-
1	27	94	91	81	80	85	75	99
2	19	93	-	-	-	-	-	-
4	17	93	86	75	93	89	57	87
5	14	93	95	73	79	94	56	99

---

[a] Feed replaced with fresh secondary effluent each day except over weekend.

[b] Determined at 600 psi with 10 GPH feed circulation velocity. Values reported are the averages of morning and afternoon samplings.

[c] One sampling per day carried out. TDS determined by residue on evaporation.

[d] Based on feed filtered through 0.45 μm Millipore filter.

[e] Formulations were those of 33A (Membrane A) and 33B (Membrane B) given in Table 1. Both membranes annealed at 85°C.

[f] Determined at 600 psi with 1000 mg/ℓ sodium chloride solution after 1 hr of testing.

TABLE 11

COMPOSITION OF SEWAGE FEEDS IN TEST NUMBERS 1 AND 2

Test Time, Days	Electrical Conductivity, μmhos cm^{-1}[a]	Concentration, mg/ℓ					
		TDS	Cl^-[a]	COD[b]	NH_4^+	NO_3^-	Total Phosphate
Test No. 1[c]							
Start (2 hrs)	1200	-	-	-	-	-	-
1	1500	1041	165	52 (64)	12	3.0	20
2	1825	1134	190	42 (50)	15	4.9	50
5	2200	-	220	50	13	5.8	53
6	2700	-	-	66	26	4.8	51
Test No. 2[d]							
Start (1 hr)	1230	-	84	-	-	-	-
1	1530	1265	138	81 (98)	12	7.1	36
2	1770	-	-	-	-	-	-
4	1555	-	190	35 (53)	13	24	35
5	1150	897	100	52 (69)	33	28	38

---

[a] Average of morning and afternoon readings.

[b] Filtered (unfiltered).

[c] See Table 9.

[d] See Table 10.

at the rate of 10 GPH and replaced periodically with fresh effluent to keep the feed concentration relatively constant.

The membrane fluxes decreased rapidly during both tests with secondary effluent. After only 1 to 2 hrs on the sewage feed, the fluxes had declined to 67 to 84% of the initial values produced with the sodium chloride solution; after 1 day they had fallen to 54 to 34% and after 5 days to 30 to 12% of the initial values. The rate of flux decline was greater with the higher-flux A-series membranes in both tests, as seen by comparing the data for each membrane in Tables 9 and 10, and the plots of log flux versus log time for the A and B-series membranes in Test No. 2 shown in Figure 2. The increase in flux decline rate which appeared to occur after the first 20 hrs of Test No. 2, shown in Figure 2, cannot be adequately explained because of insufficient data at times less than 20 hrs. This behavior, observed in subsequent tests to varying degrees, is suggestive of more than one type of fouling or a change in the fouling process taking place during the test. Similar abrupt increases in flux decline rate have been observed in long-term tests with salt solutions and have been attributed to iron deposits. It is entirely possible that inorganic deposits formed from heavy metal compounds present in the sewage effluent or introduced externally during the test were responsible for this behavior. Evidence for this hypothesis was obtained in a later test and is discussed later in this section.

The rejection behavior of the high-flux E-383-40 membranes observed in Test Nos. 1 and 2 was excellent. With the exception of a few erratic analytical results, the rejection of various components achieved during the two tests is summarized as follows: electrical conductivity, 80 to 95%; TDS, 89 to 95%; chloride, 60 to 85%; "soluble" COD, 80 to ~ 100%; ammonium ion, 77 to 94%; nitrate ion, 31 to 75%; and total phosphate, 95 to 99%. The B-series membranes, with higher initial rejection of sodium chloride, showed higher rejection of sewage components than did the A-series membranes. The drop in rejection seen at the end of Test No. 1 and not observed in Test No. 2 was expected and is attributed to boundary layer effects due to the deposit built up on the membrane as well as the increased TDS concentration of the feed and decreased flux due to fouling. The lower feed circulation velocity employed in the first test as well as the increase in TDS concentration during this test (see Table 11) are factors which could have been responsible for an increased boundary layer.

The nitrate rejections were quite variable, and similar behavior has been observed in a previous program.[14] The value of 8% nitrate rejection obtained with both membranes during the last day of Test No. 1 appears excessively low and is attributed to faulty analytical results. Cellulose acetate membranes reject nitrate ion to a somewhat lesser degree than chloride ion but the difference is exaggerated when nitrate ion is present in low concentration. Such behavior is attributed to a mixed ion effect, which has been observed to be quite marked in tests conducted with mixed feeds containing sodium chloride and sodium sulfate, in which the chloride ion rejection was reduced in the presence of sulfate. The magnitude of the effect depends both upon the sulfate-to-chloride ratio

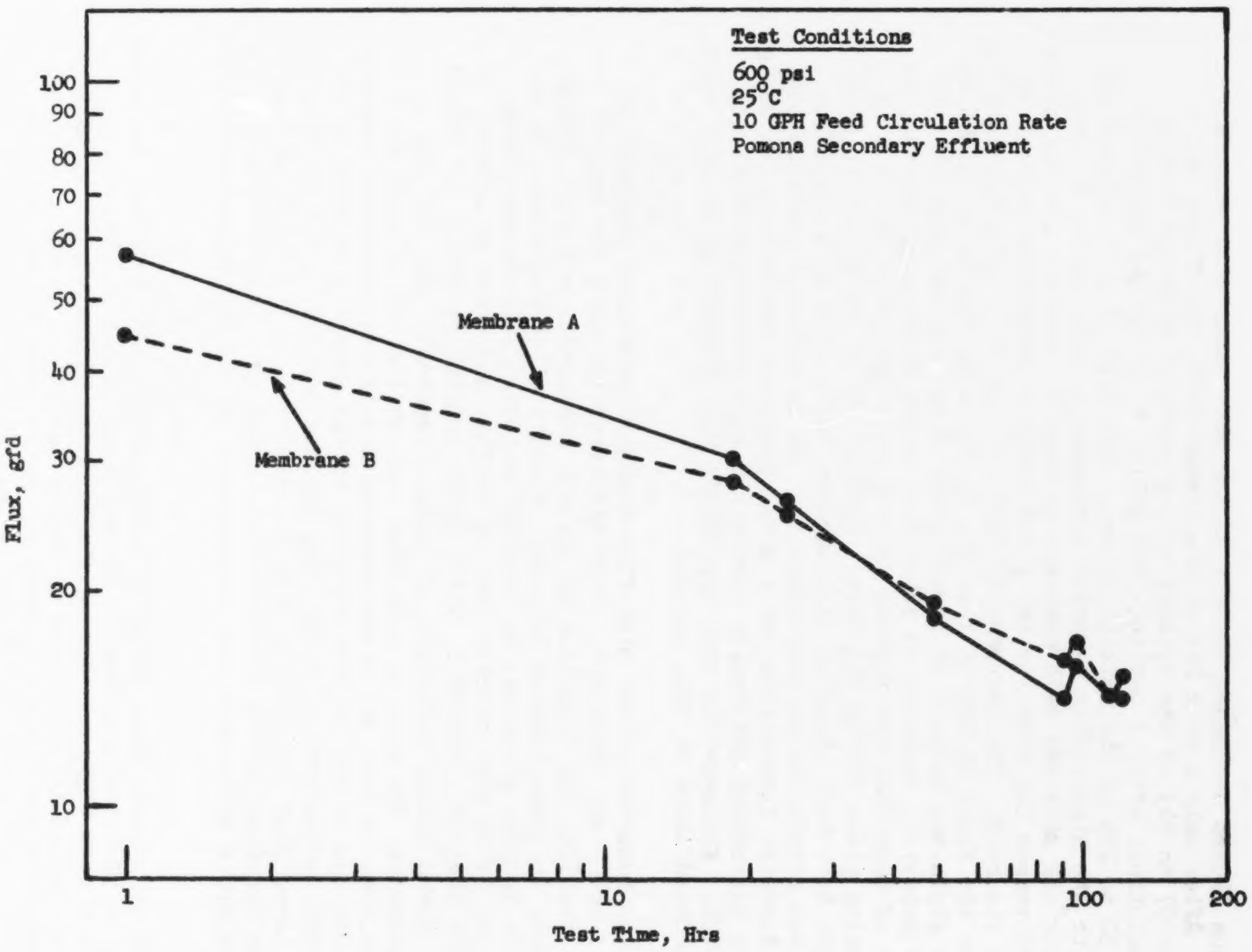

Figure 2. Flux Decline of E-383-40 Membranes
During Test No. 2

in the feed and the membrane annealing temperature. The results of a study of this phenomenon are presented and discussed in the Appendix.

With the exception of the suspect analyses, the nitrate rejections ranged between 33 and 62%. This is satisfactory for the feeds employed in this program which rarely contained greater than 20 mg/ℓ of nitrate. Higher nitrate rejections (60 to 99%) were obtained, however, in subsequent tests (Nos. 3 through 5) conducted with sewage effluents using similar E-383-40 cellulose acetate membranes as well as ds 2.55 blend membranes, as is discussed later in this section.

The high rates of flux decline observed in these first tests conducted with secondary effluent point up the seriousness of the fouling problem. That the flux decline was due mainly to fouling was indicated not only by the low flux decline slopes found previously for these membranes in tests with salt solutions, but more directly in the substantial restoration of the fluxes of the fouled membranes of Test No. 2 by cleaning. At the end of the test, a 2000 mg/ℓ aqueous solution of Procter and Gamble's enzymatic laundry presoak, Biz (pH 9.3), was circulated at ambient pressure and 50 to 60°C through the test cells for 15 min at a velocity of 10 GPH. Deionized water was then pumped through the cells at 600 psi and room temperature for an additional 15 min and the membranes tested at 600 psi with 1000 mg/ℓ sodium chloride solution. As seen by the data summarized in Table 12, the fluxes were restored to within 70 to 84% of the original values, with no decrease in rejection from that originally observed (except for one circle of membrane B which apparently was damaged). The membranes appeared visually clean after removal from the test cells. By contrast, the membranes at the end of Test No. 1, where no cleaning was employed, were covered with a substantial yellow-brown gelatinous deposit. The use of Biz in cleaning membranes has also been investigated by others and reported by Aerojet under another program.[14]

Additional specimens of the A and B-series E-383-40 cellulose acetate membranes were tested for a period of 8 days with carbon-treated secondary effluent from the Pomona Water Reclamation Plant to observe flux and rejection behavior with this higher-quality effluent. In this test (Test No. 3, see Table 13), the sewage feed was replaced daily with fresh effluent to maintain feed composition relatively constant throughout the test. The feed compositions are given in Table 14. During the first 20 to 30 hrs of Test No. 3 the rate of flux decline was less than that observed in the test conducted under similar conditions with untreated secondary effluent (Test No. 2). The rate and extent of flux decline observed after 5 days of testing in each case, however, was similar as shown by the percent of initial flux after various test times tabulated below for the B-series membranes with each effluent.

TABLE 12

CLEANING OF FOULED MEMBRANES FROM TEST NUMBER 2 WITH BIZ

Membrane Number[d]	Initial[a]		Immediately Before Cleaning[b]		After Biz Cleaning[c]	
	Flux, gfd	NaCl Rej., %	Flux, gfd	Cl^- Rej., %	Flux, gfd	NaCl Rej., %
A - 1	86	71	14	58	66	78
A - 2	80	71	17	66	60	76
A - 3	84	68	14	60	68	73
(Average)	(83)	(70)	(15)	(61)	(65)	(76)
B - 1	52	84	22	75	40	84
B - 2	60	82	10	66	48	82
B - 3	60	82	11	63	55	77
(Average)	(57)	(83)	(14)	(68)	(48)	(81)

---

[a] Determined after 1 hr of testing at 600 psi with 1000 mg/ℓ sodium chloride solution before testing with secondary sewage effluent.

[b] Data obtained at end of fifth day of Test No. 2 with secondary sewage effluent, and immediately before cleaning with Biz.

[c] Determined after testing 1 hr at 600 psi with 1000 mg/ℓ sodium chloride solution. Cleaning was carried out by circulating for 15 min at 50 to 60°C, 10 GPH and ambient pressure, a 2000 mg/ℓ solution of Biz through the test cells, followed by a 15-min wash at 600 psi with deionized water.

[d] Data given for each individual membrane circle.

TABLE 13

TESTING OF E-383-40 CELLULOSE ACETATE MEMBRANES WITH POMONA CARBON-TREATED SECONDARY EFFLUENT

TEST NUMBER 3

Test Time,[a] Days	Flux, gfd[b]	Rejection, %						
		Electrical Conductivity[b]	TDS[c]	Cl^-[b]	COD[c,d]	NH_4^+[c]	NO_3^-[c]	Total Phosphate[c]
Membrane A[e] - Initial Osmotic Properties[f]: 68 gfd flux, 71% rejection								
Start (1 hr)	62	90	-	64	-	-	-	-
1	45	91	95	67	80	85	>75	99
3	30	91	-	62	54	87	>75	98
4	25	92	91	58	57	83	>75	97
5	23	91	95	58	51	88	-	98
6	19	90	92	60	81	89	49	98
7	17	90	93	66	60	83	50	98
8	17	90	-	65	70	88	59	98
Cleaned with Biz[g] and tested at 600 psi with 1000 mg/ℓ sodium chloride: 57 gfd flux (84% initial), 76% rejection (107% of initial).								
Membrane B[e] - Initial Osmotic Properties[f]: 68 gfd flux, 76% rejection								
Start (1 hr)	65	92	-	67	-	-	-	-
1	52	93	97	70	42	91	>75	98
3	35	93	-	68	53	95	>75	95
4	27	94	91	62	72	94	>75	99
5	25	92	96	58	44	-	-	99
6	20	92	93	66	80	91	63	99
7	19	90	94	68	67	88	55	99
8	19	91	-	69	57	91	63	98
Cleaned with Biz[g] and tested at 600 psi with 1000 mg/ℓ sodium chloride: 62 gfd flux (91% of initial), 83% rejection (109% of initial).								

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[a] Feed replaced daily with fresh effluent.

[b] Determined at 600 psi with 10 GPH feed circulation velocity; 3 circles of each membrane tested and averaged. Values reported are the averages of morning and afternoon samplings. Sewage feed pH maintained at 5.00 ± 0.25.

[c] One sampling per day carried out. TDS determined as residue on evaporation.

[d] Based on feed filtered through 0.45 μm Millipore filter.

[e] Formulations were those of 33A and 33B given in Table 1. Both membranes annealed at 85°C.

[f] Determined at 600 psi with 1000 mg/ℓ sodium chloride solution after 1 hr of testing.

[g] Thirty-minute wash with 2000 mg/ℓ Biz solution (pH 9.3 to 9.5) at room temperature, 600 psi, 12 GPH.

TABLE 14

FEED COMPOSITION - TEST NUMBER 3 WITH POMONA CARBON-TREATED SECONDARY EFFLUENT

Test Time, Days	Electrical Conductivity,[a] μmho cm^{-1}	Concentration, mg/ℓ					
		TDS	Cl^-[a]	COD[b]	NH_4^+	NO_3^-	Total Phosphate
Start (1 hr)	1025	-	94	-	-	-	-
1	1175	808	91	21 (21)	24	0.4	32
3	1430	-	103	31 (32)	19	0.4	42
4	1300	838	86	33 (33)	2	0.4	50
5	1175	813	74	47 (56)	25	0.4	38
6	1350	820	87	31 (31)	20	3.5	38
7	1250	864	118	31 (35)	21	17	36
8	1400	-	115	28 (31)	21	23	36

---

[a] Average of morning and afternoon samples.

[b] Filtered (unfiltered).

	Flux Retention (% of Initial Flux)	
Test Time with Sewage	Secondary Effluent (Test No. 2)	Carbon-Treated Secondary Effluent (Test No. 3)
Start	81	96
1 hr	79	96
5 days	25	37
8 days	-	28

This similarity is also seen by comparison of the log flux-log time plots given in Figure 3. An increase in the rate of flux decline was observed after about 30 hrs in Test No. 3 with carbon-treated secondary effluent at least as marked at that seen during Test No. 2 with untreated secondary effluent. This behavior with carbon-treated effluent was rather surprising, in view of its higher quality compared with untreated secondary effluent. These results together with results obtained in tests conducted with carbon-treated secondary effluent under a previous program,[14] are highly suggestive of extraneous matter, such as airborne dust, in the feed.

The rejection behavior of the membranes observed during the test with carbon-treated secondary effluent (Test No. 3) was similar to that observed with untreated secondary effluent (Test No. 2) except for the lower "soluble" COD rejection (generally 50 to 80% vs. 80 to 100% as shown in Tables 10 and 13). This difference is illustrated by the fact that higher product COD values were obtained in Test No. 3 than in Test Nos. 1 and 2. The lower "soluble" COD rejection may have resulted from the presence of a highly permeable organic or oxidizable inorganic component present in the carbon-treated secondary effluent.

Cleaning of the fouled membranes at the end of Test No. 3 was conducted by circulating a 2000 mg/ℓ solution of Biz through the test cells for 30 min at 600 psi and room temperature at a flow rate of 12 GPH. The membrane fluxes were restored to 84% (membrane A) and 91% (membrane B) of their initial values with increases in salt rejection over that originally observed for each membrane (see Table 13).

In view of the effectiveness of Biz cleaning in restoring the flux of fouled membranes, observed after Test Nos. 2 and 3 with secondary and carbon-treated secondary effluents, respectively, a test was carried out with more frequent cleaning. Specimens of Membranes A and B, annealed at 85°C, were again employed and the test (Test No. 4) was conducted at 600 psi with Pomona secondary sewage effluent. The cells were cleaned intermittently by treatment at 600 psi and 12 GPH circulation rate for 30 min with a 2000 mg/ℓ solution of Biz at room temperature. The highly promising results of this test are summarized in Tables 15A and 15B, for membranes A and B, respectively. The composition of the sewage feeds used are summarized in Table 16. During the first 94 hours of the test, when the Biz cleaning was carried out every 24 hours, the flux of Membrane

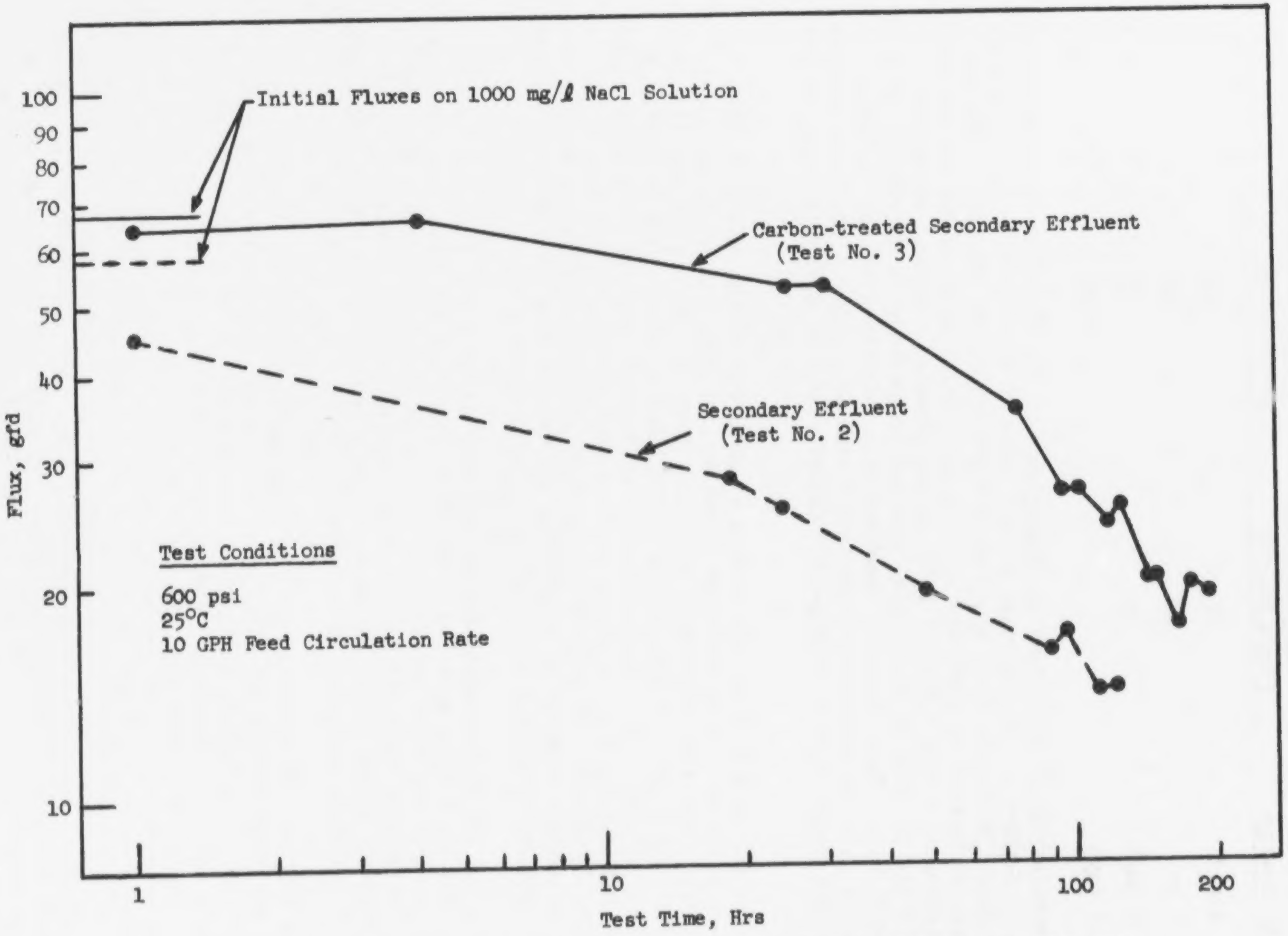

Figure 3. Flux Decline of B-Series E-383-40 Membranes with Different Effluents

TABLE 15A

TESTING OF E-383-40 MEMBRANES WITH SEWAGE UTILIZING PERIODIC BIZ CLEANING

TEST NUMBER 4 - MEMBRANE A

Date	Time	Flux,[a] gfd	Rejection, %[a]						Comments
			Electrical Conductivity	Cl^-	COD[b]	NH_4^+	NO_3^-	Total Phosphate	
3/17/70	1100		94 gfd flux, 72% rejection						1000 mg/ℓ NaCl
3/17/70	1200	73	-	-	-	-	-	-	Start with secondary effluent
3/17/70	1300	68	92	68	-	-	-	-	
3/17/70	1600	64	93	67	-	-	-	-	
3/18/70	0900	56	93	66	100	92	80	97	
3/18/70	1130	73	89	63	73	86	79	97	Biz Cleaning[c]
3/18/70	1330	64	91	-	-	-	-	-	
3/18/70	1600	74	91	76	-	-	-	-	Add fresh secondary effluent
3/19/70	0900	51	90	69	96	90	91	98	
3/19/70	1000	68	89	-	94	87	76	97	Biz Cleaning[c]
3/19/70	1200	65	90	73	-	-	-	-	Add fresh secondary effluent
3/19/70	1600	56	89	73	-	-	-	-	
3/20/70	0900	51	92	64	83	93	72	98	
3/20/70	1200	66	90	-	-	-	-	-	Biz Cleaning[c]
3/20/70	1600	67	91	-	-	-	-	-	
3/21/70	1000	48	91	-	82	96	84	98	Add fresh secondary effluent
3/22/70	1000	43	90	-	-	-	-	-	
3/23/70	0900	42	90	-	81	90	95	98	
3/23/70	1100	61	87	-	-	-	-	-	Biz Cleaning[c]
3/23/70	1200	58	89	-	79	87	45	99	Start with primary effluent
3/23/70	1600	31	90	-	-	-	-	-	
3/23/70	2200	21	88	-	-	-	-	-	
3/24/70	0900	13	88	-	61	88	67	>99	
3/24/70	1200		61 gfd flux, 79% rejection						Biz wash[d], then 1000 mg/ℓ NaCl
3/24/70	1300	49	88	-	-	-	-	-	Add fresh primary effluent
3/24/70	1600	33	88	-	-	-	-	-	
3/24/70	2200	21	86	-	-	-	-	-	
3/25/70	0900	17	86	-	59	85	67	98	
3/25/70	1200		40 gfd flux, 85% rejection						Biz wash[e], then 1000 mg/ℓ NaCl

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[a] Determined at 600 psi with 10 GPH feed circulation velocity. Values reported are the averages of 3 test circles. Sewage feed pH maintained at 5.00 ± 0.25.

[b] Based on feed filtered through 0.45 μm Millipore filter.

[c] 2000 mg/ℓ aqueous solution of Biz circulated at 12 GPH, room temperature and 600 psi for 30 min, then switch to previous feed.

[d] Washed for 30 min as in C above, then reduced pressure to ambient for 1 min and continue with 15 min wash at 600 psi as before.

[e] Washed as in d above except for only 15 min before pressure cycling.

TABLE 15B

TESTING OF E-383-40 MEMBRANES WITH SEWAGE UTILIZING PERIODIC BIZ CLEANING

TEST NUMBER 4 - MEMBRANE B

Date	Time	Flux,[a] gfd	Rejection, %[a] Electrical Conductivity	Cl^-	COD[b]	NH_4^+	NO_3^-	Total Phosphate	Comments
3/17/70	1100	62 gfd flux, 87% rejection							1000 mg/ℓ NaCl
3/17/70	1200	50	-	-	-	-	-	-	Start with secondary effluent
3/17/70	1300	48	96	79	-	-	-	-	
3/17/70	1600	48	95	84	-	-	-	-	
3/18/70	0900	44	96	79	97	92	>98	99	
3/18/70	1130	51	94	68	82	93	>98	99	Biz Cleaning[c]
3/18/70	1330	50	95	-	-	-	-	-	
3/18/70	1600	51	95	86	-	-	-	-	Add fresh secondary effluent
3/19/70	0900	42	95	84	95	90	>96	99	
3/19/70	1000	51	94	-	81	91	>95	99	Biz Cleaning[c]
3/19/70	1200	49	94	84	-	-	-	-	Add fresh secondary effluent
3/19/70	1600	45	94	78	-	-	-	-	
3/20/70	0900	42	96	73	89	96	91	99	
3/20/70	1200	46	95	-	-	-	-	-	Biz Cleaning[c]
3/20/70	1600	47	96	-	-	-	-	-	
3/21/70	1000	41	96	-	88	93	>97	99	Add fresh secondary effluent
3/22/70	1000	38	95	-	-	-	-	-	
3/23/70	0900	37	95	-	85	91	95	>99	
3/23/70	1100	46	94	-	-	-	-	-	Biz Cleaning[c]
3/23/70	1200	44	95	-	82	86	42	>99	Start with primary effluent
3/23/70	1600	30	95	-	-	-	-	-	
3/23/70	2200	20	95	-	-	-	-	-	
3/24/70	0900	14	94	-	66	91	85	>99	
3/24/70	1200	46 gfd flux, 92% rejection							Biz wash[d], then 1000 mg/ℓ NaCl
3/24/70	1300	44	94	-	-	-	-	-	Add fresh primary effluent
3/24/70	1600	30	94	-	-	-	-	-	
3/24/70	2200	18	94	-	-	-	-	-	
3/25/70	0900	14	93	-	61	92	75	>99	
3/25/70	1200	35 gfd flux, 93% rejection							Biz wash[e], then 1000 mg/ℓ NaCl

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[a] Determined at 600 psi with 10 GPH feed circulation velocity. Values reported are the averages of 3 test circles. Sewage feed pH maintained at 5.00 ± 0.25.

[b] Based on feed filtered through 0.45 μm Millipore filter.

[c] 2000 mg/ℓ aqueous solution of Biz circulated at 12 GPH, room temperature and 600 psi for 30 min, then switch to previous feed.

[d] Washed for 30 min as in c above, then reduced pressure to ambient for 1 min and continue with 15 min wash at 600 psi as before.

[e] Washed as in d above except for only 15 min before pressure cycling.

TABLE 16

COMPOSITION OF PRIMARY AND SECONDARY EFFLUENT FEEDS IN TEST NUMBER 4

Feed	Date	Time	Electrical Conductivity, μ mho cm^{-1}	Concentration, mg/ℓ				
				Cl^-	COD[a]	NH_4^+	NO_3^-	Total Phosphate
Secondary Effluent	3/17/70	1200	1360	80	-	-	-	-
Secondary Effluent	3/17/70	1600	1380	85	-	-	-	-
Secondary Effluent	3/18/70	0900	1440	100	41 (53)	21	4.4	50
Secondary Effluent	3/18/70	1130	1625	160	65 (69)	24	6.2	50
Secondary Effluent	3/18/70	1600	1350	110	-	-	-	-
Secondary Effluent	3/19/70	0900	1460	145	43	14	9.8	35
Secondary Effluent	3/19/70	1000	1200	100	37	16	7.5	36
Secondary Effluent	3/19/70	1600	1300	90	-	-	-	-
Secondary Effluent	3/20/70	0900	1500	-	42	19	7.8	40
Secondary Effluent	3/21/70	1000	1400	-	51	20	12	42
Secondary Effluent	3/22/70	1000	1630	-	-	-	-	-
Secondary Effluent	3/23/70	0900	1700	-	37 (45)	18	18	50
Secondary Effluent	3/23/70	1100	1500	-	-	-	-	-
Primary Effluent	3/23/70	1200	1350	-	64 (149)	20	3.6	38
Primary Effluent	3/24/70	0900	1550	-	46 (114)	31	2.7	36
Primary Effluent	3/24/70	1600	1550	-	-	-	-	-
Primary Effluent	3/25/70	0900	1800	-	70 (135)	19	11	37

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[a] Filtered (unfiltered).

A was maintained at 48 to 73 gfd (66 to 100% of the initial flux on secondary effluent) and that of Membrane B at 41 to 51 gfd (82 to 102% of the initial flux on the sewage). Of equal note was the low rate of flux decline observed with the secondary effluent between Biz washings, this being comparable or lower than that observed in the test with carbon-treated secondary effluent (see Table 13). Between each of the first three Biz cleanings the flux of the A membrane decreased by 23 to 30% and that of the B membrane by 11 to 18%, compared with 26% and 20% decreases in flux of the A and B membranes, respectively, during the first 24 hours of testing with carbon-treated effluent. During the 4th and 5th day of the test, when no Biz cleaning was employed, the fluxes of the A and B membranes decreased by only 12 and 10%, respectively, compared with decreases of 33% observed with each membrane during a corresponding 48-hour period in Test No. 3 with carbon-treated effluent. The effectiveness of the periodic cleaning in maintaining high flux levels with secondary effluent is illustrated graphically in Figure 4 by log flux-log time plots for the B-series membranes in Test Nos. 2 and 4. Several plausible, but speculative, explanations can be offered for the relatively low rates of flux decline between Biz cleanings in Test No. 4. First, it is possible that the Biz treatment imparted some antifouling properties to the membrane through adsorption of enzymes on its surface. Second, the quality of the secondary effluent used during this test was unusually high. Third, contamination of the feed by extraneous matter, such as airborne dust from the laboratory ventilation system, which may have contributed to the flux decline in the previous tests, may have been less in Test No. 4.

Although the rejection behavior of both membranes during Test No. 4 with secondary effluent was excellent, Membrane B was again superior. The B-series membranes, which gave initially lower flux and higher rejection of sodium chloride than the A-series membranes, consistently exhibited better rejection behavior as well as lower flux decline when tested against sewage effluents. The rates of flux decline of the A and B-series membranes in Test No. 4 during the first 24 hours of the test, between cleanings and over the duration of the test with secondary effluent are compared graphically in Figure 5. Again, as in the previous tests, the rate of flux decline was greater with the membrane producing higher initial flux. Slopes of -0.081 for the A-membrane (initial flux on sodium chloride of 94 gfd) and -0.054 for the B-membrane (initial flux on sodium chloride of 62 gfd) on Pomona secondary effluent are obtained for the lines defined by the initial flux values on sodium chloride for each membrane and the flux values obtained on the secondary effluent immediately after each cleaning. These slopes yield extrapolated year-end post-cleaning flux values of 44 and 38 gfd, respectively, for the A and B-membranes. Still more favorable flux decline slopes of -0.071 and -0.033, respectively, were calculated for the A and B-membranes using all of the points shown in Figure 5. Even these results, however, do not reflect the full potential of these membranes, since similar membranes exhibited intrinsic flux decline slopes of only -0.04 and -0.02, respectively, in long-term tests with salt solution. Therefore, still greater productivity might be realized by further improvement of the cleaning procedure, feed pretreatment, etc.

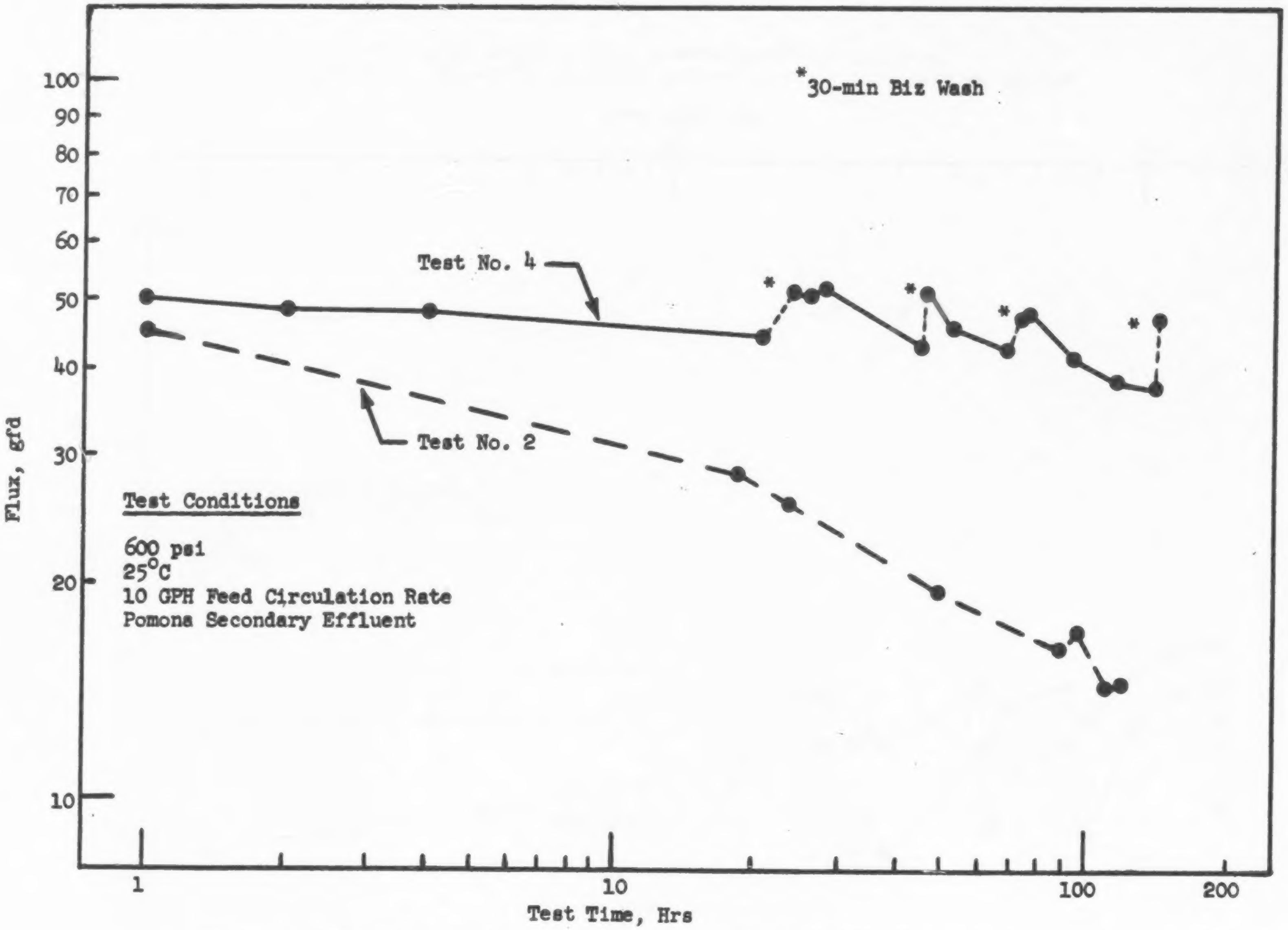

Figure 4. Effect of Periodic Biz Cleaning on Performance of B-Series E-383-40 Membranes with Secondary Effluent

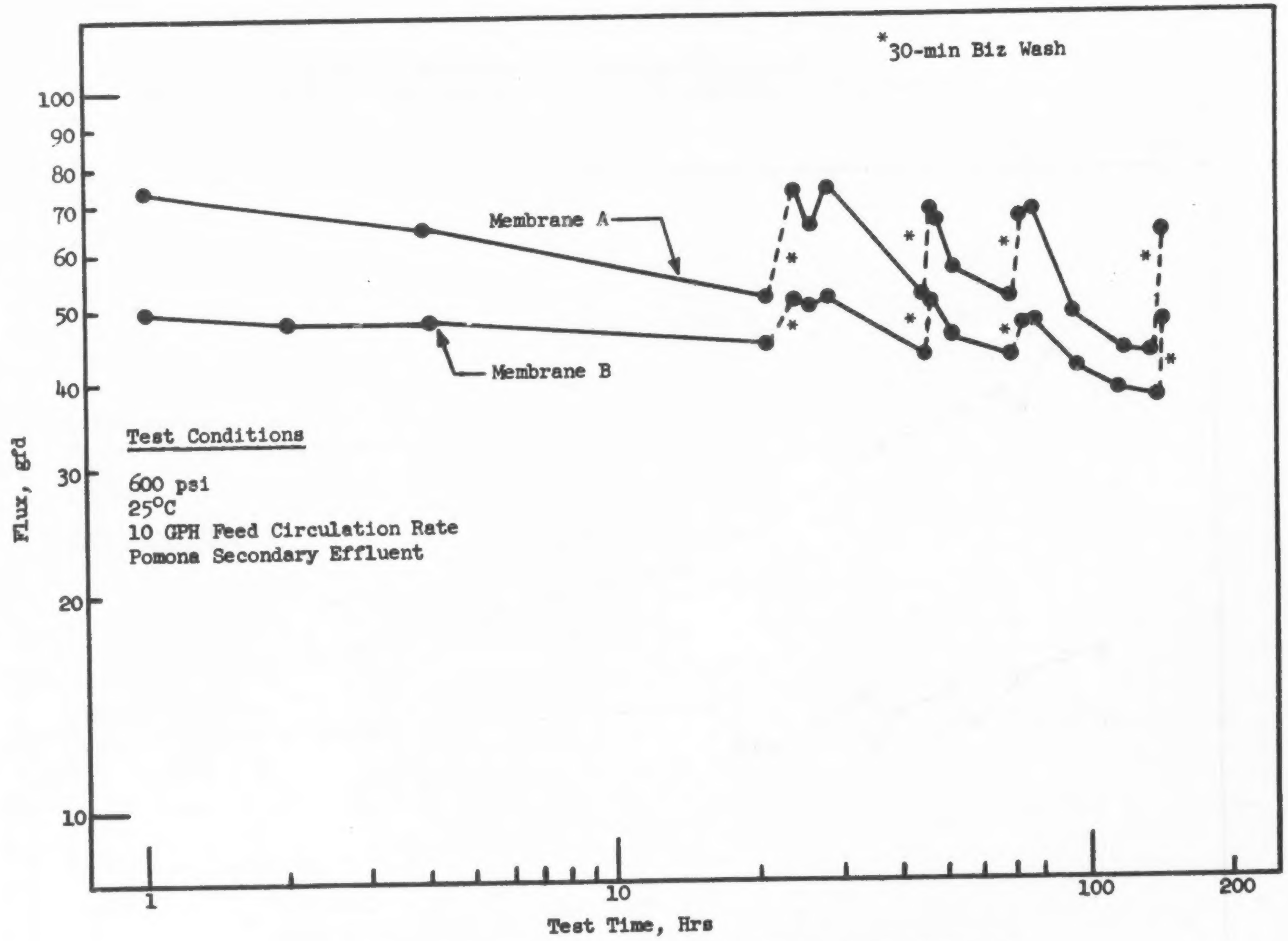

Figure 5. Effect of Membrane Initial Flux on Flux Decline During Test Number 4 with Pomona Secondary Effluent

During the last 2 days of Test No. 4, Pomona primary sewage effluent was used as feed to observe membrane performance and the efficacy of Biz cleaning with this lower quality effluent. The data obtained in this experiment are shown in Tables 15A and 15B. As expected, the rate of flux decline was considerably greater with the primary effluent than that observed with secondary effluent (72 to 79% decline for Membrane A and 70% decline for Membrane B in 21 hrs between cleanings as compared with 23 to 30% and 11 to 18% declines, respectively, during corresponding 24-hr periods with secondary effluent); and the cleaning procedure was less effective with the primary than with the secondary effluent. In the first cleaning cycle with primary effluent, fluxes were not restored appreciably when circulating the Biz solution under pressure but were restored immediately after reducing the pressure to ambient for several minutes. The fluxes were not completely restored to the original peak values after the second cleaning attempt. At this point the test was terminated and the membranes removed for examination. All of the membrane circles were found to contain an opaque bluish-white surface deposit, the color apparently caused by the bluing agent present in Biz. The amount of the deposit appeared by inspection to vary inversely with the final flux produced by each circle. Of equal significance was the observation of the residue of a second type of deposit, more characteristic of the organic matter deposited from sewage. This transparent, gelatinous, yellow-brown material was present in small quantity on top of the bluish-white surface deposit on one or two of the membranes. The presence of this second type of deposit did not relate to final membrane flux and since it was present in small quantity on only certain membranes it appears to be readily removable by the Biz cleaning treatment.

A sample of the bluish-white deposit was collected, dried, pyrolyzed in a furnace at 1000°F and the residue submitted for flame emission analysis to determine major metallic constituents. The results of the analysis are summarized below.

Element	%, Based on Oxides
Fe	3.7
Al	36.3
Mg	1.5
Si	2.3
Na	25.6

No phosphorus was detected in the flame emission spectrum, and a qualitative test for sulfate was negative, eliminating the possibility that the deposit had been comprised substantially of phosphates or calcium sulfate. Precipitation of polyvalent metal phosphates during the Biz treatment had been suspected, in particular, since the phosphate content of Biz is 18.7% based on elemental phosphorus.

On the basis of the above analyses, and its relatively dense physical form, the original blue-white membrane deposit appears to have been inorganic in nature, and comprised of a refractory metal oxide mixture. Its origin appears to have been extraneous having been introduced into the primary effluent in the form of airborne dust either at the Pomona Water Reclamation Plant or in the laboratory during the test. The latter alternative seems to be a good possibility, the prime suspect being fine particles of insulation material (e.g., mineral wool) from the air ducts of the laboratory ventilation system entering the uncovered feed tanks. Such contamination may also have been responsible for the increased flux decline with time in Test Nos. 1, 2, and 3. Accordingly, the feed tanks were kept covered during the remaining tests with sewage described below.

The results obtained in the tests of the E-383-40 cellulose acetate membranes with various sewage effluents were very encouraging with respect to rejection behavior and the utility of membrane cleaning in moderating the flux decline due to fouling. At the same time, they were instructive as to the extent of the fouling problem in reducing the productivity of membranes having high intrinsic flux and flux stability. It was therefore of interest to evaluate and compare the performance of the other two membrane types, namely the ds 2.55 blend and crosslinked CAM-360, in similar tests with sewage effluent. The two remaining tests, Nos. 5 and 6 described below, were conducted for this purpose, using untreated secondary effluent as the feed.

Specimens of ds 2.55 blend membranes cast from the formulations designated 35A and 35C in Table 4 and annealed at 85°C were tested for a period of 17 days at 600 psi with Pomona secondary effluent. The results obtained in this test, designated Test No. 5, are summarized in Table 17. The feed compositions are given below.

Test Time, Days	Electrical Conductivity, μ mho cm^{-1}	Concentration, mg/ℓ				
		COD				
		Soluble	Total	NH_4^+	NO_3^-	Total Phosphate
Start (1 hr)	1460	40	40	19	17	33
6	1450	36	54	14	29	36
12	1690	35	54	16	44	38
17	1400	-	-	-	-	-

The test data indicate relatively low rates of flux decline (for secondary effluent) throughout much of the test period, as well as generally very high rejection of all components analyzed. The low COD rejections obtained on the 6th and 12th days of the test were inconsistent with the high rejections of other components observed on those days as well as the high COD rejections obtained at the beginning of the test. This discrepancy could have been caused by faulty analyses, sample contamination or the presence of highly permeable oxidizable components in the feeds used on those days.

TABLE 17

TESTING OF DS 2.55 BLEND MEMBRANES WITH POMONA SECONDARY EFFLUENT

TEST NUMBER 5

Test Time, Days	Flux,[a] gfd	Rejection, %[a]					
		Electrical Conductivity	COD		NH_4^+	NO_3^-	Total Phosphate
			Soluble[b]	Total			
Membrane 35A[c] - Initial Osmotic Properties[a,d]. 68 gfd flux, 77% rejection							
Start (1 hr)	51	94	100	100	96	99	99
1	53	95	-	-	-	-	-
2	45	94	-	-	-	-	-
5[e]	43	95	-	-	-	-	-
6	40	95	-	-	-	-	-
12	38	94	51	68	91	99	99
14[e]	37	95	56	72	87	99	99
17	32	95	-	-	-	-	-
After cleaning with Bis[f]: 57 gfd flux, 89% sodium chloride rejection.[a,d]							
Membrane 35C[c] - Initial Osmotic Properties[a,d]: 57 gfd flux, 80% rejection							
Start (1 hr)	46	90	100	100	93	99	99
1	42	96	-	-	-	-	-
2	36	95	-	-	-	-	-
5[e]	33	95	-	-	-	-	-
6	28	95	-	-	-	-	-
12	26	94	47	65	91	99	99
14[e]	24	95	48	66	92	99	99
17	21	92	-	-	-	-	-
After cleaning with Bis[f]: 47 gfd flux, 84% sodium chloride rejection.[a,d]							

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[a] Determined at 600 psi. Data reported are averages of 3 test specimens.

[b] Based on feed filtered through 0.45 μm Millipore filter.

[c] Formulation 35A (parts by wt) - cellulose triacetate A-432-130B, 6; cellulose acetate E-398-3, 14; dioxane, 45; acetone, 40; maleic acid, 6; acetamide, 10. Formulation 35C - same except used 14 parts propionamide instead of acetamide. Membranes annealed at 85°C.

[d] Determined with 1000 mg/ℓ sodium chloride solution at 600 psi after 1-hr test period.

[e] Feed replaced with fresh effluent.

[f] Carried out at end of test by circulating a 2000 mg/ℓ aqueous solution of Bis at room temperature, 600 psi and 10 GPH.

Cleaning of the membranes with Biz at the end of Test No. 5 increased the fluxes to more than 80% of their initial values determined with 1000 mg/ℓ sodium chloride solution and revealed an improvement in salt rejection. The flux decline behavior of the membranes during the test is shown graphically by log flux-log time plots in Figure 6. The rate of flux decline on the secondary effluent was similar for the two membranes, and was approximately linear after the first 24 hours of operation. Slopes of -0.030 to -0.032 of the lines drawn between the flux values determined with 1000 mg/ℓ sodium chloride solution at the beginning of the test and at the end of the test after Biz cleaning are even better than the corresponding value of -0.054 obtained in Test No. 4 for an E-383-40 cellulose acetate membrane of comparable initial flux (B-membrane). These values correspond to less than 25% loss in flux after the first year of operation. As in the case of the E-383-40 membranes, the intrinsic flux decline slopes of these membranes (-0.011 to -0.013) with salt solution indicate that improved control of fouling will yield still greater flux stability in the treatment of sewage.

A final test (Test No. 6) was conducted with the best examples of each of the three promising high-flux membrane types examined in the program in the same test apparatus using a common secondary effluent feed, to obtain a more direct comparison of their performance on sewage. The test was conducted with 2 circles of each membrane type at 600 psi for a period of 6 days and yielded the results summarized in Table 18 and presented graphically in Figure 7. For the CAM membrane, formulation 32E in Table 6 was cast at room temperature, annealed at 70°C and crosslinked at that temperature for 10 min as previously described. The E-383-40 membrane was cast from the formulation designated 33A in Table 1 and annealed at 85°C; and the blend membrane was cast from the formulation designated 35A in Table 4 and annealed at 85°C. Each of the membranes was tested for 1 hr with both sodium chloride and sodium sulfate before testing with the sewage feed. The sewage feed was replaced every other day with fresh effluent and the flux and electrical conductivity of the feed and product were measured twice daily.

All three membranes at the beginning of Test No. 6 gave high sodium sulfate rejections (97 to 99%). The CAM membrane exhibited the best rejection characteristics of the three - 92% of sodium chloride, 99% of sodium sulfate and 95 to 97% of TDS in sewage. Its initial flux on secondary effluent was 57 gfd falling to 29 gfd after 6 days on the sewage. The E-383-40 membrane exhibited the highest initial flux (85 gfd) on salt solution but the greatest flux decline on secondary effluent of the three (see Figure 7) producing after 6 days on the sewage only 22 gfd flux. Although its rejection performance was greater than the minimum requirement, the E-383-40 membrane, giving the lowest rejections of sodium chloride (70%) and sodium sulfate (97%), also gave the lowest rejection of TDS (87 to 92%) with the sewage. The blend membrane produced the lowest initial flux (50 gfd) on salt solutions and exhibited a flux decline rate on the sewage comparable to that of the crosslinked CAM membrane, giving after 6 days a flux of 20 gfd. The blend membrane ranked intermediate in rejection performance among the three membranes

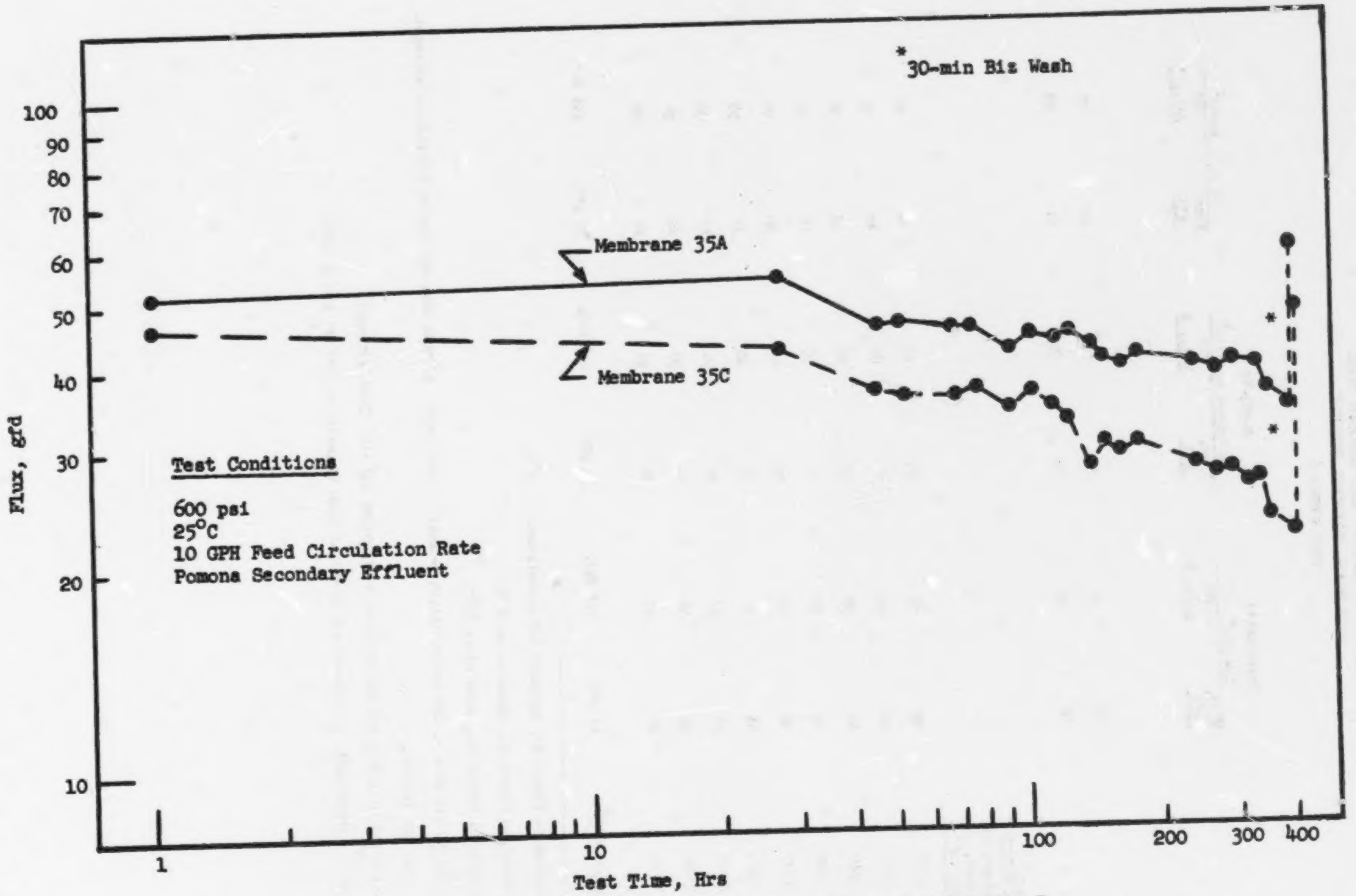

Figure 6. Flux Decline of DS 2.55 Blend Membranes During Test Number 5

TABLE 18

COMPARATIVE TEST OF THREE MEMBRANE TYPES WITH POMONA SECONDARY EFFLUENT

TEST NUMBER 6

		Crosslinked CAM-360[a]		E-383-40 Cellulose Acetate[b]		DS 2.55 Blend[c]	
		Flux, gfd	TDS Rej., %	Flux, gfd	TDS Rej., %	Flux, gfd	TDS Rej., %
Initial Osmotic Properties[d,e]							
1000 mg/ℓ NaCl		69	92	85	70	47	79
1000 mg/ℓ Na_2SO_4		66	99	83	97	51	98
Secondary Effluent[d,f]							
Test Time, Hrs	Electrical Conductivity of Feed, μ mho cm^{-1}						
1	1525	57	95	71	87	41	91
3	1525	56	96	66	88	40	92
20	1600	42	97	43	90	33	94
27	1700	44	97	43	90	34	94
44	1700	38	97	36	89	30	94
51	1550	41	97	36	92	31	95
116	1700	34	97	25	91	23	96
123	1500	32	96	24	90	22	94
140	1500	29	97	22	92	20	96
Cleaned with Biz,[g] Tested with 1000 mg/ℓ NaCl[d]		43 gfd	95% Rej.	32 gfd	85% Rej.	28 gfd	93% Rej.

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[a] Cast from 32E formulation (Table 6), annealed and crosslinked at 70°C.

[b] Cast from 33A formulation (Table 1), annealed at 85°C.

[c] Cast from 35A formulation (Table 4), annealed at 85°C.

[d] Testing conducted at 600 psi with 10 GPH recirculation velocity. Two circles of each membrane tested and results averaged.

[e] Determined after 1-hr test periods.

[f] Sewage feed pH maintained at 5.00 ± 0.2 and replaced every other day with fresh effluent.

[g] Aqueous solution of Biz (2000 mg/ℓ circulated for 30 min at room temperature, 600 psi and 10 GPH).

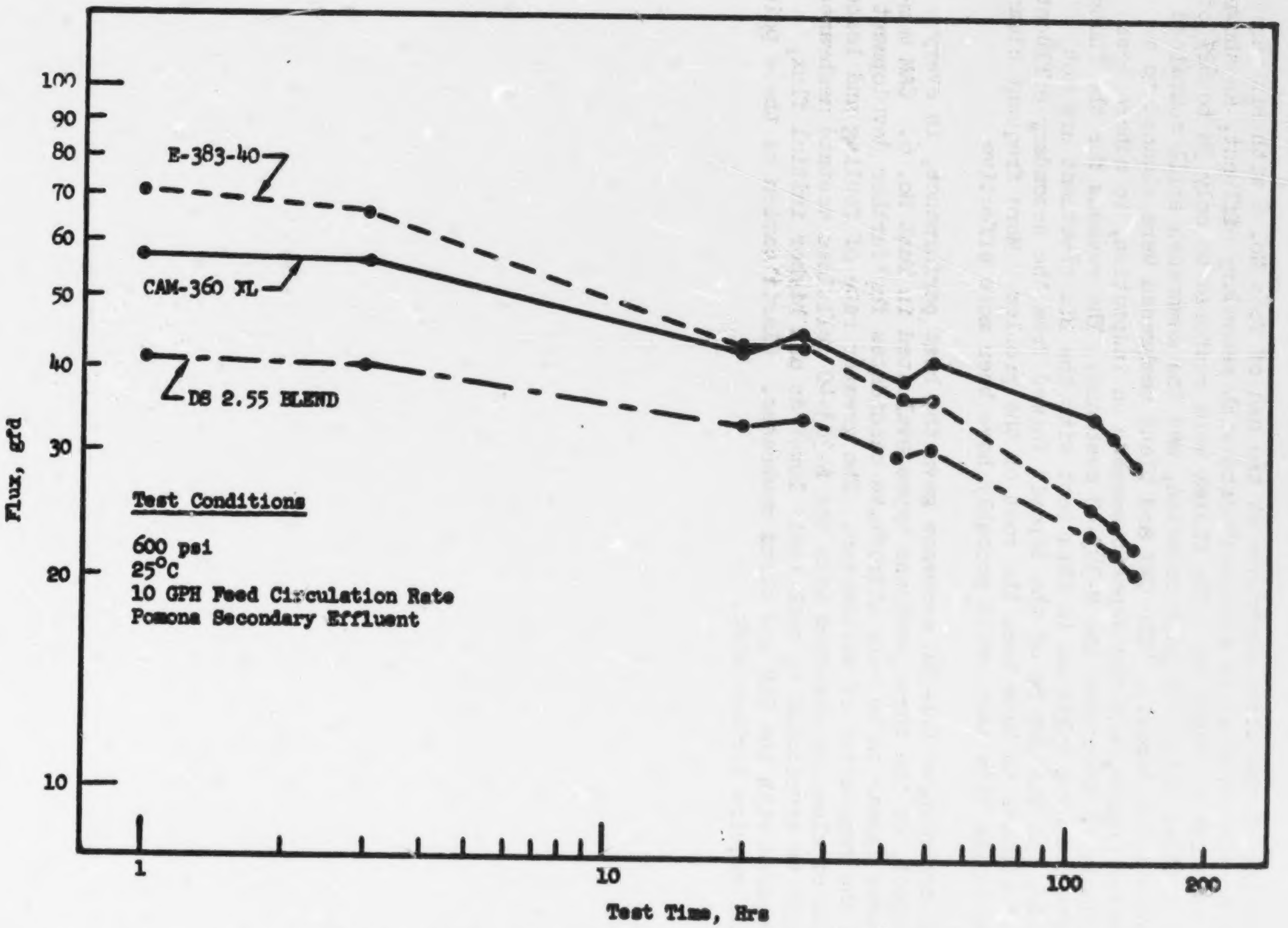


Figure 7. Flux Decline of the Three Membrane Types During Test Number 6

with 91 to 96% TDS rejection on the sewage.

Cleaning of the three membranes at the end of Test No. 6 with Biz was not as effective as in previous tests with secondary effluent, as shown by the data in Table 18. The fluxes were restored to only 38 to 62% of the initial values on salt solution, and the membranes still contained a gelatinous deposit. The CAM and blend membranes were cleaned to a greater degree, and the deposit seemed, on inspection, to adhere less strongly to them than the E-383-40 membrane. The reasons for the incomplete cleaning achieved in this test with the Biz treatment are not clear, but the nature of the deposit formed from the secondary effluent used appears to have been the root of the problem. More frequent cleaning during this test would probably have been more effective.

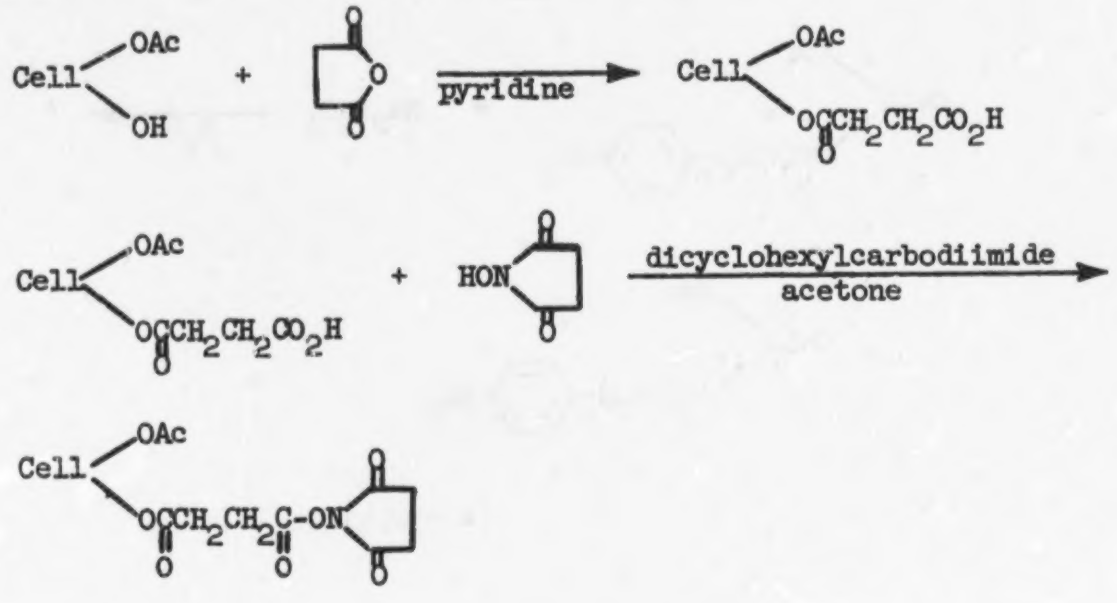
The crosslinked CAM-360 membrane gave the best performance, in every respect, of the three membrane types evaluated in Test No. 6. CAM membranes appear to be very attractive candidates for further development in the renovation of wastewater. The greater rate of fouling and lesser ease of cleaning observed with the E-383-40 cellulose acetate membranes could be attributed to both their lower ds and higher initial flux, compared with the CAM and blend membranes. Clarification of these points will require further work.

VI. MEMBRANES RESISTANT TO COLLOID FOULING

METHODS OF ATTACHMENT OF ENZYMES TO CELLULOSIC MEMBRANES

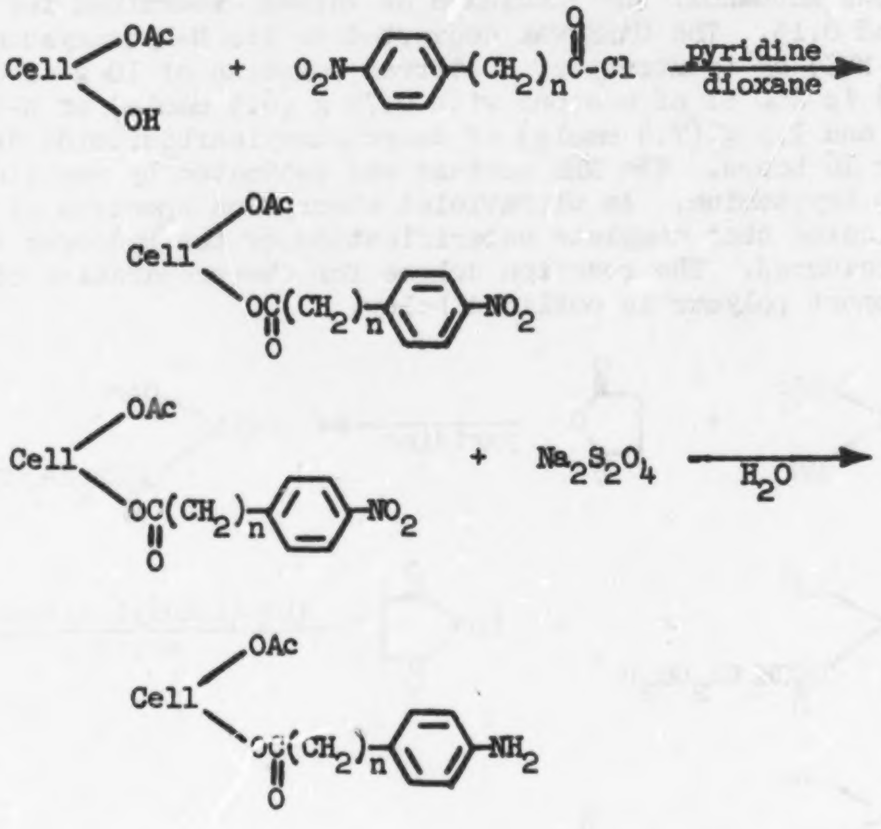
Several coupling reactions were available for attaching enzymes to reactive polymers. Two types of reactive polymers which offered versatile intermediates were investigated, namely, carboxyl-substituted and arylamine-substituted cellulose acetates. The carboxyl groups could be converted to an activated ester and coupled with enzyme amino groups, while arylamino groups could be converted either to reactive isothiocyanates or diazonium salts, which would couple with enzyme amino or phenolic groups, respectively.

An activated ester group which appeared to fit the requirements of water-stability and mild reaction conditions was reported by Anderson and co-workers,[15] who utilized N-hydroxysuccinimide esters of amino acids for peptide synthesis. Amide formation between an amine and the activated ester occurs in aqueous solution at pH 8.0, conditions which are ideal for enzyme attachment. Accordingly, cellulose acetate hydrogen succinate (CAHS) was prepared by treating 212 g of cellulose acetate (Eastman Type E-400-25, acetyl ds 2.38) with 24 g of succinic anhydride in 1ℓ of pyridine. The product was purified by precipitation from 2ℓ of acetone in 7ℓ of 50% aqueous methanol; the succinate ds values determined for two batches were 0.17 and 0.15. The CAHS was converted to its N-hydroxysuccinimide ester (CAHS-NHS) by treatment of a stirred solution of 10 g of CAHS (6.5 meq of COOH) in 250 ml of acetone with 0.75 g (6.5 mmole) of N-hydroxysuccinimide and 1.5 g (7.4 mmole) of dicyclohexylcarbodiimide at room temperature for 16 hours. The NHS content was estimated by reaction of the polymer with tryptamine. An ultraviolet absorption spectrum of the product indicated that complete esterification of the hydrogen succinate groups had occurred. The reaction scheme for the preparation of this reactive support polymer is outlined below.



Aminoaryl-substituted support polymers were prepared by acylation of cellulose acetate with a nitroaryl acid chloride and reduction of the nitro group to an amine. Sixty grams of cellulose acetate Type E-400-25 was acylated with 18 g of p-nitrobenzoyl chloride in 500 ml of dioxane and 25 ml of pyridine at 100° for 5 hours. The p-nitrobenzoyl (PNB) ds of the resulting polymer, found by ultraviolet spectrophotometry, was 0.28. An earlier batch, prepared using an impure sample of p-nitrobenzoyl chloride, had a PNB ds of 0.08.

Reduction of 10 g of the lower ds material with 2 g of sodium hydrosulfite in 150 ml of water at 25°C produced cellulose acetate p-aminobenzoate (CAPAB) with a PAB ds of 0.05. The product from a similar reduction of the higher ds material was not sufficiently soluble in dioxane (or other suitable solvents) to permit determination of the PAB ds by ultraviolet spectrophotometry. Acylation of 60 g of E-400-25 cellulose acetate with 22 g of 4-(4'-nitrophenyl)butyryl chloride in 500 ml of dioxane and 25 ml of pyridine produced cellulose acetate 4-(4'-nitrophenyl)butyrate (CAPNPB) with a PNPB ds of 0.22, measured by ultraviolet spectrophotometry. Ten grams of this polymer was reduced with 10 g of sodium hydrosulfite in 150 ml of 67% aqueous ethanol at 75°C. The only solvent found for the product was dimethyl sulfoxide; the (p-aminophenyl)butyryl (PAPB) ds was found by ultraviolet spectrophotometry to be 0.18. The reaction scheme for the preparation of aminoaryl support polymers is summarized below:



(n = 0,4)

ATTACHMENT OF ENZYMES TO BULK POLYMERIC SUPPORTS

Before preparing membranes having attached enzymes, the methods of attachment were investigated by coupling of the enzymes with the bulk support polymers. It has been generally noted, in studies of insoluble enzymes, that a greater reduction in activity (compared with the native enzyme) is observed with macromolecular substrates than with monomeric substrates.[6] This effect is generally ascribed to steric hindrance by the polymeric support. During investigation of methods of attachment, the resulting insoluble enzymes were assayed by kinetic procedures utilizing a monomeric substrate; this allowed a rapid evaluation of the efficacy of the attachment procedures.

After samples of native trypsin, chymotrypsin, and papain were assayed for activity against monomeric substrates, it appeared that trypsin could be assayed most conveniently and with the greatest sensitivity. Trypsin was therefore used in the majority of insoluble enzyme preparations, and the activity was measured by ultraviolet spectroscopic determination of the rate of hydrolysis of benzoyl arginine ethyl ester (BAEE).[16] The protein content of the insoluble enzyme preparations was determined by a modification of Habeeb's 2,4,6-trinitrobenzenesulfonic acid (TNBS) method for monitoring protein hydrolysis.[17] The insoluble enzymes were hydrolyzed in 6 N hydrochloric acid, and an aliquot was neutralized and treated with TNBS at pH 9.0. After acidification, the concentration of the colored reaction product was determined spectrophotometrically. Calibration curves for this analytical method were prepared using known concentrations of each enzyme.

When 50 mg of trypsin was stirred with 500 mg of CAHS-NHS in 10 ml of 1% aqueous sodium bicarbonate solution at 25°C for 4 hours, an insoluble enzyme containing 3.2% protein was obtained. The activity of this material, as measured by BAEE assay, was 6% of the activity of a like amount of native trypsin. When the reaction temperature was reduced to 0 to 4°C the protein content was almost the same, 2.8% but the activity of the insoluble enzyme was 13-17% of that of native trypsin.

Since a proteolytic enzyme such as trypsin loses activity in solution due to self-digestion, it was thought that even greater retention of enzymatic activity might be obtained by inhibiting the enzyme during the attachment reaction. When attachment was carried out at 0 to 4°C in the presence of 0.1 M benzoylarginine, which inhibits BAEE hydrolysis by trypsin, the apparent protein content of the insoluble enzyme was 4.0%. Based on the observed 4.0% protein content, the enzymatic activity measured by BAEE was 7% of that of native trypsin. (The TNBS reagent used to determine protein content measures the concentration of free amino groups. If benzoyl arginine reacted with the CAHS-NHS, arginine would be liberated upon acid hydrolysis, and an erroneously high apparent protein content would be observed.) Because of these poor results, no further investigation of the use of inhibitors during attachment was carried out.

The preparation of insolubilized chymotrypsin and papain was carried out by reaction of the native enzymes at room temperature with bulk CAHS-NHS.

These preparations were attempted before the discovery, with trypsin, that lower reaction temperatures (i.e., 0 to 4°C) resulted in greater retention of enzymatic activity after attachment. The insoluble CAHS-chymotrypsin obtained was found to contain 4.5% protein; its activity was 2.8% of the activity of the native enzyme, as measured by hydrolysis of tyrosine ethyl ester.[16] The sample of native papain used was found to contain only 24% protein, and the sample of insoluble CAHS-papain obtained contained only 0.8% protein. In view of the low purity and activity toward BAEE hydrolysis of the native papain, no attempt was made to assay the activity of the insoluble enzyme. Although a purified native papain would probably give improved results, further efforts in the preparation of an enzymatic membrane were limited to trypsin, as described below.

Although the lack of solubility of the aminoaryl derivatives of cellulose acetate in the usual membrane casting solvents may present some difficulty in preparing membranes from these polymers, an insoluble enzyme was prepared by diazonium coupling of CAPAPB to trypsin. The protein content of this material was 2.1%; the activity, compared with native trypsin, was nil (probably less than 0.05%). This lack of activity may have resulted from the inactivation of trypsin by the polymeric diazonium salt, a low enzymatic activity having been reported for insoluble trypsin prepared by coupling with a diazotized copolymer of p-amino-DL-phenylalanine and L-leucine.[6] Diazonium coupling, therefore, is apparently not a feasible method for preparing trypsin membranes.

Attachment of an enzyme to an insoluble carrier frequently results in a shift in the pH optimum (the pH at which maximal activity occurs). The shift may be to either more positive or more negative values, depending on the electrostatic charge on the carrier. Since hydrolysis of N-hydroxysuccinimide ester groups which were not involved in binding the enzyme would result in a negative charge on the carrier, it was of interest to determine whether a shift in optimum pH had occurred. The variation with pH in activity of the insoluble trypsin, relative to native trypsin at pH 8.0, is shown by the following data.

pH	Activity
7.0	7%
8.0	17%
9.0	14%

The optimum pH for insoluble CAHS-trypsin is apparently between 7 and 9, not significantly different from that of the native enzyme.[16]

To provide a measure of the effectiveness of insoluble trypsin in hydrolizing proteinaceous colloids, a sample of the insoluble enzyme (CAHS-trypsin) was assayed with casein as substrate, using the TNBS procedure of Habeeb.[17] The sample of insoluble trypsin which had shown an activity toward BAEE hydrolysis of 13 to 17% of that of the native trypsin was 2.9% as active as the native enzyme when assayed with casein. This lower activity toward a macromolecular substrate is in agreement with literature reports on other insoluble enzyme preparations.[6]

PREPARATION OF ENZYME-COUPLED MEMBRANES

A membrane intended for enzyme coupling was prepared by machine casting at room temperature from a solution containing (by weight) CAHS-NHS, 10 parts; propionamide, 7 parts; maleic acid, 3 parts; dioxane, 20 parts; acetone, 20 parts. This membrane was gelled at 0°C after less than 5 sec drying time and stored under methanol at 5°C until ready for use. Reaction of a sample of the CAHS-NHS membrane with tryptamine in the same manner described previously for the bulk polymer indicated that 74% of the NHS groups remained intact after casting. A second portion of the membrane was annealed in water for 3 min at 74°C; tryptamine analysis of this sample indicated that 43% of the NHS groups originally present in the polymer remained after both casting and annealing. These experiments, together with the successful attempts at enzyme coupling described below, demonstrated that although the very reactive CAHS-NHS polymer was susceptible to hydrolysis, membranes could be fabricated from it under normal conditions which contained sufficient reactive sites for enzyme attachment.

An enzyme-coupled membrane was prepared by immersing a 27.5 cm^2 specimen of the unannealed CAHS-NHS membrane in a solution of 50 mg of trypsin in 5 ml of 2% aqueous sodium bicarbonate for 70 hrs at 4°C. Following this treatment, the membrane was thoroughly washed, in succession, with 0.001 N hydrochloric acid, 0.01 M borate buffer (pH 9.0) and water. The resulting membrane was found to contain 1.1% protein. A portion of the membrane which had been left in contact with the trypsin solution for 10 days before washing was found to have a protein content of 1.4%, indicating that most of the enzyme attachment was complete after 70 hrs.

A sample of the enzymatic membrane prepared by reaction with trypsin for 70 hrs was cut into 1 to 2-mm squares, and its enzymatic activity assayed with BAEE. The activity of enzyme attached to the membrane toward BAEE hydrolysis was found to be 2.5% of that of the native trypsin. After 4 days in aqueous suspension (pH ca. 6, 25°C) at room temperature, the enzymatic activity was 1.7% compared to native trypsin (68% of its initial activity). Bar-Eli and Katchalski[18] have examined the stability of trypsin solutions as a function of pH. They found that a solution of trypsin containing 25 g enzyme per ml lost 60% of its activity in 25 hours at pH 6 and 25°C. Their result indicates that native trypsin would retain only 2 to 3% of its activity under conditions where the enzyme membrane retained 68% of its initial activity. It is clear from this experiment that attachment to the CAHS-NHS membrane stabilized the trypsin toward loss of activity, which presumably occurs by self-catalyzed hydrolysis. Such a stabilizing effect has been observed for other insoluble enzyme preparations, including other trypsin derivatives.[6] These results indicate that enzymes having greater stability than trypsin should be investigated for attachment to membranes, in order to insure maximum retention of activity of enzymatic membranes during long periods of reverse-osmosis operation.

The trypsin membrane described above was prepared with both sides of the membrane exposed to the trypsin solution. For prevention of colloid fouling, only enzymes on the active layer side will be effective. Furthermore, the substructure of the enzyme is much more porous than the active layer, and enzymes could possibly have penetrated and become attached within the substructure. Interior enzymes would contribute to the observed protein content, but might be less reactive than surface enzymes since the substrate would have to diffuse into the membrane and products would have to diffuse out. To examine an enzyme membrane with essentially only surface enzymes a portion of membrane was masked with Mylar film and waterproof tape to allow only the active layer to contact the trypsin solution. The resulting membrane contained 0.22% protein; its activity relative to native trypsin was 1.8%, slightly less than the membrane with trypsin on both sides. The lower activity of the membrane-bound enzyme relative to the enzyme attached to bulk polymer under the same conditions can probably be ascribed to the effect of surface area. Manecke has reported[19] that increasing the surface area of synthetic polymers used as enzyme carriers increases the amount of enzyme bound, and also increases the reaction rate of the insoluble enzyme with its substrate. Thus, trypsin attached to the membrane, especially on the active layer side with its smaller surface area, is somewhat less reactive than trypsin attached to the fibrous bulk polymer.

Verification that trypsin had become attached to both sides of the earlier membrane and only one side of the latter one, was obtained by staining both membranes with Pink RL dye, a protein-specific stain. Excess dye was removed with ethanol and sections of the two membranes were examined at 420X magnification under reflected light. The pink dye was concentrated at both surfaces of the first membrane, with only a faint color in the interior. In the second membrane (active layer side only), however, the dye was concentrated at the active layer surface, with essentially no color at the other surface and very little color in the interior.

A demonstration of hydrolysis by the enzyme-coupled membrane of a colloidal protein, such as casein, was not practical. Based on the BAEE activity of the enzymatic membranes and the bulk enzymes, hydrolysis of casein by either membrane would not be measurable by the assay procedures available. It has been demonstrated (vide supra) that bulk CAHS-trypsin is capable of effecting hydrolysis of a model proteinaceous colloid, namely casein. Moreover, the trypsin membranes have been shown to possess enzymatic activity by hydrolysis of BAEE. The colloid concentrations to be found in secondary effluent probably do not exceed 5 mg/ℓ,[5] a concentration which is one or two orders of magnitude below the sensitivity of the methods used to assay casein hydrolysis. While the enzymatic activity on the active layer is small, a small activity may well be sufficient to prevent fouling by wastewater colloids at these low concentrations. Tests of the enzymatic membrane with sewage are required to answer this question.

MEMBRANES FROM CELLULOSE ACETATE HYDROGEN SUCCINATE

Prior to preparing enzyme membranes, preliminary membrane formulation studies were conducted with cellulose acetate hydrogen succinate (CAHS). These were not extensive enough to optimize the formulation, but did provide a formulation adequate for the highly swollen membranes used in preparing trypsin membranes. Some reverse osmosis data were also obtained on these membranes which may indicate another method of preventing fouling by colloids.

The best reverse osmosis performance with CAHS membranes was attained with a formulation containing (by weight): CAHS, 20 parts; propionamide, 14 parts; maleic acid, 6 parts; dioxane, 45 parts; and acetone, 40 parts. Membranes were cast from this solution at room temperature with less than 5 sec drying time and gelled at 0°C. After annealing at 74°C this membrane exhibited a flux of 13 gfd with 89% rejection when tested at 600 psi with 1000 mg/ℓ sodium chloride feed solution. After two hours on secondary effluent the flux was 46 gfd with 72% conductivity rejection. This increase in flux was accompanied by a change in the recirculating feed from an initial pH of 7.0 to pH 8.2. After 3 hours the pH was adjusted with 6 N sulfuric acid to pH 4.9. During the next 18 hours the pH rose to 6.8, with a flux of 27 gfd at 78% rejection. After 24 hours the membrane was subjected to a Biz wash. After the Biz wash the flux was increased only to 32 gfd with 32% rejection, declining to 18 gfd and 21% rejection over a period of three days. Visual examination after the test showed very little of the slimy deposits generally accumulated in that length of time.

The large changes in flux and rejection observed during the above test can probably be ascribed to the effect of the CAHS carboxyl groups. The charge density on the membrane would be expected to increase with increasing pH in the pH range encountered above, which would alter the permeability to water and ionic species. The increase in pH which occurred during the test is also probably due to the presence of carboxyl groups.

The highly alkaline conditions of the Biz wash apparently resulted in degradative damage to the active layer, as evidenced by the large decrease in conductivity rejection.

To ascertain whether the negatively charged CAHS membrane might have inherent antifouling characteristics another membrane from a similar formulation (using 10 parts of acetamide instead of propionamide) was tested for 16 days on Pomona secondary effluent, maintaining the feed pH at 4.7 to 5.5 by periodic addition of dilute sulfuric acid. Initially the flux was 15.5 gfd, with 80% conductivity rejection. After 6 days the flux was unchanged, and the rejection was 87%. The flux dropped to 13.5 gfd after 8 days and to 6 gfd after 16 days. The complete absence of flux decline over the first 6 days, however, suggests that the CAHS membrane may have inherent fouling resistance. The colloids involved in fouling may be negatively charged at the pH maintained during this test, and would thus be repelled by a membrane of like charge. This possibility should be pursued further.

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APPENDIX

EFFECT OF SULFATE ON CHLORIDE REJECTION IN MIXED FEEDS

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APPENDIX

EFFECT OF SULFATE ON CHLORIDE REJECTION IN MIXED FEEDS

In brackish-water tests carried out several years ago, abnormally low nitrate rejection was observed in feed waters containing sodium nitrate in the presence of a large excess of calcium sulfate. It was considered of practical interest, during this program, to determine the extent to which this effect applied to sodium chloride rejection in mixed feeds containing sodium chloride and sodium sulfate since such feeds were used in evaluation of membranes in the program.

A crosslinked CAM-360 membrane, cast at -10°C, and annealed at 80°C, was tested at 200 psi against a series of feeds, all of which had the same osmotic pressure, in which the ratio of sodium sulfate to sodium chloride was varied. Included in the series were feed solutions containing either solute alone. The results, summarized in Table A-1, indicate a strong effect of sulfate on chloride rejection, the chloride rejection decreasing with increased sulfate-to-chloride ratio in the feed. The chloride rejection was observed to decrease from a value of 85% with the feed containing sodium chloride alone to 56% with the feed containing the highest ratio of sulfate to chloride. The sulfate rejection also was affected by variation in feed composition, increasing with increased sulfate-to-chloride ratio.

A second series of tests was carried out to determine to what extent the mixed ion rejection effect was a function of membrane annealing temperature. To this end, membranes were cast from a 1:1 blend (ds 2.63) formulation, annealed at various temperatures and tested at 150 psi successively against the following feed solutions:

Feed No. 1 - 250 mg/ℓ NaCl, 750 mg/ℓ Na_2SO_4
Feed No. 2 - 1000 mg/ℓ NaCl
Feed No. 3 - 1000 mg/ℓ Na_2SO_4

The results of these tests, summarized in Table A-2, indicate that the extent to which sodium chloride rejection decreases in the presence of sodium sulfate is greater the lower the annealing temperature for a given membrane formulation. With the unannealed membrane, sodium chloride rejection fell from a value of 52% with pure sodium chloride solution (feed No. 2) to 11% with the mixed feed (feed No. 1), a decrease of 78%. The percentage decrease fell consistently as the annealing temperature was increased, so that with the 70°C membrane, sodium chloride rejection was reduced from 93% with the sodium chloride feed to 85% with the mixed feed, a drop of only 10%.

TABLE A-1

EFFECT OF FEED COMPOSITION ON REJECTION BEHAVIOR OF CAM MEMBRANE

Feed Composition, mg/ℓ				
NaCl	Na_2SO_4	Flux,* gfd	NaCl* Rejection, %	Na_2SO_4* Rejection, %
1310	0	32.7	85.2	-
960	640	36.8	74.0	90.6
486	1500	39.7	70.0	94.2
61	2500	38.4	55.7	97.3
0	3500	35.8	-	96.1

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*Measured at 200 psi after 2-hour test period using membrane annealed at 80°C. The casting formulation was as follows (amounts of ingredients in parts by weight): CAM-360, 10; acetone, 40; maleic acid, 14; water, 10. Crosslinking was carried out after annealing by immersion of the membranes for 3 min at 90°C in a solution containing 0.037 **M** of potassium persulfate and 0.038 **M** of sodium bisulfite.

TABLE A-2

EFFECT OF ANNEALING TEMPERATURE ON REJECTION CHARACTERISTICS OF BLEND MEMBRANES

Annealing[a] Temp., °C	Feed[b]	Flux,[c] gfd	NaCl Rejection,[c] %	Na_2SO_4 Rejection,[c] %	% Reduction of NaCl Rejection by Na_2SO_4
25 (unannealed)	1	35.8	11.3	99.9	78.3
	2	36.4	52.0	-	-
	3	36.2	-	98.1	-
50	1	22.3	38.4	99.7	44.2
	2	23.2	68.8	-	-
	3	22.5	-	98.6	-
60	1	14.2	68.1	99.9	19.3
	2	13.4	84.4	-	-
	3	13.7	-	98.3	-
70	1	8.7	83.8	99.7	10.0
	2	8.1	93.1	-	-
	3	8.3	-	98.0	-

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[a] Membrane formulation (parts by wt) - E-398-3, 10; A-432-130B, 10; dioxane, 55; acetone, 35; methanol, 9; maleic acid, 3.

[b] Feed No. 1 - 250 mg/l sodium chloride, 750 mg/l sodium sulfate
Feed No. 2 - 1000 mg/l sodium chloride
Feed No. 3 - 1000 mg/l sodium sulfate

[c] Determined at 150 psi after 2-hour test periods.

The reduction of chloride and nitrate ion rejections in the presence of other ions, such as sulfate, does not appear to be of serious consequence in the treatment of wastewater by reverse osmosis because the rejections obtained are still high enough to produce product water with acceptably low concentrations of these ions. The rejection of organic components, furthermore, should not be affected by the presence of ionic components, since the former are, in almost all cases, nonionic in nature.

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27 Abstract
Stable, high-flux membranes were sought for use in the renovation of wastewater by reverse osmosis. Cellulose ester membranes were formulated to produce fluxes greater than 60 gal/ft^2-day which would not decrease by more than 20% after the first year of operation, and reject at least 60% of sodium chloride and 95% of sodium sulfate when tested at 600 psi with 1000 ppm feed solutions. The target osmotic performance was achieved with each of three membrane types: A cellulose diacetate of moderately-low acetyl content, a cellulose triacetate-diacetate blend, and crosslinked cellulose acetate methacrylate. The intrinsic flux stabilities of these membranes extrapolated to flux losses of only 12 to 18% after the first year of operation. The fluxes of these high-performance membranes declined rapidly in bench-scale tests with secondary sewage effluent but were restored to within 80 to 90% of the initial values after cleaning with an enzymatic laundry presoak (Biz). Daily cleaning by this technique maintained the fluxes at a nearly constant level over a 5-day test period. The rejection of sewage components by the high-flux membranes was excellent. Techniques were explored for attachment of proteolytic enzymes to cellulose acetate membranes to render them resistant to colloid fouling. The proteolytic enzyme trypsin was chemically attached to the active layer surface of a membrane prepared from the N-hydroxysuccinimide ester of cellulose acetate hydrogen succinate. The resulting enzymatic membrane displayed hydrolytic activity.

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